A GEOCHEMICAL INVESTIGATION OF THE WATERS AND SEDIMENTS OF DE HOOP VLEI, BREDASDORP DISTRICT, SOUTH AFRICA

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Preface

The experimental work described in this thesis was carried out in the Department of Geological Sciences , University of Cape Town, during 1996 and 1997, under the supervision of Associate Professor James Willis and Dr Martin Fey.

The study represents original work by the author and has not been submitted for degree purposes to another university. Where use has been made of the work of others, it has been duly acknowledged in the text.

Johann Lanz

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The Environmental Geochemistry class of 1996 for the times we shared before I was left behind

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Abstract

De Hoop Vlei is a saline coastal lake situated 53 kilometres north-east of Cape Agulhas in the Western Cape Province of South Africa. It is probably of estuarine origin but is now separated from the sea by mobile sand dunes and, therefore, has no surface outflow. Inflow to the vlei is from a catchment area of approximately 1200 km^2 in which intensive grain farming is practised. The vlei is situated within the De Hoop Nature Reserve and its ecological value, particularly as a breeding ground for water birds, has been recognised in its designation as an international RAMSAR conservation site. Agricultural practices in the catchment have been identified as a potential threat to the ecology of the vlei.

The overall objective of this study was to provide a geochemical characterisation of De Hoop Vlei. It focused on identifying the geochemical factors and processes which control the water chemistry of the vlei and attempted to identify any influence of agricultural activities on water quality. This was achieved through a geochemical interpretation of the results obtained from analyses of water and sediment samples collected during the study. Use was also made of Department of Water Affairs and Forestry monitoring data in order to examine long term behaviour of the system, particularly with respect to the effect of evaporative concentration on water composition. Furthermore, chemical equilibrium was modelled, using the geochemical model MINTEQA2, in order to give an indication of processes likely to occur in the water as well as the behaviour of certain possible pollutants in the vlei.

Water and sediment core samples, collected during two separate sampling trips, were taken along the entire length of the vlei and some water samples were taken in the catchment. Interstitial waters were obtained by suction from sediment cores. Samples of secondary precipitates, found along the edge of the vlei, were also taken. The following laboratory analyses were performed on water samples: pH, EC, alkalinity, major cations and anions, dissolved P, fluoride, and the trace metals Fe, Mn, Al, Ni, Cu, Zn, and Pb. The following laboratory analyses were performed on sediment samples: pH of wet and dried sediments, organic C content, carbonate content, total elemental concentrations of major and trace elements, mineralogy, clay percentage and extractable P, Zn and K. Scanning electron microscopy and mineralogical analyses were performed on samples of secondary precipitates.

The water chemistry of De Hoop Vlei is characterised by a high degree of spatial and temporal variation. In general the waters are alkaline with pH values between 8 and 10 and are either saline, with Na and Cl as dominant ions, or non saline with higher proportions of dissolved Ca and carbonate. The EC of vlei water samples varied between 86 and 3070 mS/m.

Interstitial water samples had a higher salinity and lower pH than the overlying bulk waters. The water of De Hoop Vlei would generally be classified as hyposaline having a salinity between 3 and 20 g/L but in the southern parts of the vlei the waters become mesosaline (>20 g/L) during dry periods.

Spatial and temporal variation of water chemistry in the vlei is adequately explained by the mixing of high and low salinity inflow waters and by evaporative concentration. It is possible to distinguish three broad types of surface waters in the study area: (1) water characteristic of influent rivers; (2) spring water from a limestone environment; and (3) brines evolved by evaporative concentration of influent waters. Spring waters have low salinity, low Mg/Ca ratios and lower pH values. Evaporative concentration leads to increases in all these parameters. The cation concentration sequence changes from Na > Ca > Mg > K for the spring waters to Na > Mg > K > Ca for the brines. The majority of vlei waters have the anion sequence $Cl > SO_4 > (HCO_3 + CO_3)$.

During the evolution of the vlei water by evaporative concentration a small amount of Na is lost from the water column relative to chloride. This unusual behaviour of Na can possibly be explained by stripping of Ca and Mg from exchange sites due to their precipitation as carbonates, which enables Na to exchange for these cations on exchange sites in the sediments. The other major solutes are all removed to a significant extent during evaporative concentration. The stripping of divalent cations from exchange sites may also facilitate the effective uptake of K during evaporative concentration. The evolution of the De Hoop water is likely to follow path 1 of the Hardie-Eugster model of brine evolution because the equivalent concentration of alkalinity is higher than that of Ca. This means that the Ca concentration will become very small with increased evaporative concentration.

The results of P analyses indicated large differences in the concentrations of dissolved P between the waters of the catchment and those of the vlei. Surface waters of the catchment had P concentrations as high as 2.75 mg/L while all vlei waters sampled at the same time were below 0.04 mg/L. The results suggest that it is likely that P enrichment of surface waters is occurring in the catchment, although these levels may be natural. The results also show that P is effectively being removed from the water column in the vlei. The concentration of P in the interstitial waters was far higher than in the overlying bulk waters. Nitrogen was only detected in interstitial water samples where it occurred in the form of NH_4^+. It was below detection in all other samples.

Concentrations of trace metals in surface waters were low (< 0.04 mg/L) as was expected due

to the high pH and high carbonate content of the system. The modelling results of hypothetical pollution inputs into the vlei water indicated that the vlei is likely to effectively buffer the concentrations of the trace metals Pb and Zn at low levels, and thereby limit ecological effects resulting from their introduction into the vlei.

Calculations using MINTEQA2 indicated that all water samples were supersaturated with respect to calcite , aragonite and dolomite. Waters subjected to a high degree of evaporative concentration were also supersaturated with respect to a number of other Mg carbonate minerals. Precipitation of calcite, aragonite, monohydrocalcite, nesquehonite and sepiolite was indicated as feasible in De Hoop Vlei. The waters were also strongly supersaturated with respect to two apatite minerals, hydroxy-apatite and an F and CO_3 substituted apatite.

Four major components of the De Hoop sediments were identified. These were carbonate minerals, resistate minerals of sand-and silt size, clay minerals and organic matter. The proportions of these vary along the length of the vlei. Reducing conditions were evident in much of the sedimentary environment of De Hoop Vlei.

Sediments in the south of the vlei are dominated by aragonite with lesser amounts of calcite. These minerals are likely to be controlling Ca concentrations in the waters of De Hoop Vlei. It is likely that significant quantities of Ca and carbonate are being transferred from the water column to a solid phase in the sediments in this part of the vlei. In the littoral zone, secondary precipitates of two unusual carbonate minerals, monohydrocalcite and nesquehonite, were identified. The reason for the precipitation of these minerals instead of aragonite or calcite is unknown.

The clay content of sediments increases markedly in a northerly direction along the length of the vlei. Sediment clays were found to be mineralogically uniform and dominated by micas with smaller amounts of kaolinite. Both these minerals are likely to be derived directly from the soils and rocks of the catchment. Aluminium, Fe, Ti and K and the trace elements Ba, Rb, V, Cr, Zn, Ni, Y, Pb, Sc, Co, Nb, and Th showed strong positive correlations with clay percentage and are therefore likely to occur almost exclusively in the clay mineral fraction of the sediments.

Magnesium is associated with both carbonates and with clay minerals. In the southern part of the vlei it is probably present as magnesium carbonate minerals, while in the north, where the clay content is high and carbonates are low, most magnesium is probably associated with clay minerals. The elements most strongly associated with the organic matter fraction are S

and U.

The accumulation of P, K and Zn, which are all potentially augmented by agricultural activities, was compared in sediments in the southern and northern parts of the vlei to give an indication of any enrichment due to agricultural contamination. The results showed no clear indication of any such contamination although some K enrichment may be occurring in the northern parts where the river enters the vlei.

It was concluded that the water chemistry of De Hoop Vlei is controlled by the composition of different influent waters as well as by geochemical processes that occur during evaporative concentration. Important processes in this regard are likely to be the precipitation of carbonates and other minerals, sorption on clay surfaces and redox reactions in the sediments. The concentrations of a number of major ions as well as trace metals and P are likely to be buffered in the vlei water due to saturation and, therefore, equilibrium with a solid phase. Both trace metals and P have low solubilities in the De Hoop Vlei water. The results of the study showed no clear indication of agricultural contamination in the vlei or catchment.

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Chapter 1 Introduction

1.1 Introduction and motivation for the study

De Hoop Vlei is a saline coastal lake situated 53 kilometres north-east of Cape Agulhas in the Western Cape Province of South Africa (Fig. 1.1). It is classified as an endorheic coastal lake (Noble & Hemens, 1978) and due to its levels of salinity may be classified as saline. It is probably of estuarine origin and was separated from the sea by mobile coastal sands closing off the mouth of the estuary (Walsh, 1968 cited in Coetzee, 1986). It is now separated from the sea by 2.5 km of mobile sand dunes and therefore has no surface outflow. Inflow to the vlei is from a catchment area of approximately 1200 km^2 which extends 65 km inland in an area where intensive grain farming is practised. The main river draining the catchment is the Sout River which flows into the vlei from a north-westerly direction. A tributary, the Potberg River, drains the catchment from the east. In addition to these inflows the vlei receives water from ground water seepage which results in a number of springs emerging along the north-eastern edge of the vlei. Photographs showing different views of the vlei are given in Figures 1.4 - 1.6.

The vlei is situated within the De Hoop Nature Reserve which encompasses a variety of different ecosystems focusing on the preservation of the coastal fynbos biome. The ecological value of the vlei itself as a breeding ground for water birds has been recognised, and it has consequently been designated as an internationally recognised RAMSAR site for the conservation of water fowl. Agricultural contamination has been recognised as a potential threat to the ecology of the vlei (PD Toens and Associates, 1994a; Scott, 1995).

A geochemical investigation of De Hoop Vlei is interesting and important for a number of reasons. There are few geochemical data available on wetland systems generally in Southern Africa and particularly on saline water bodies (Seaman *et al.*, 1991). There is also a world-wide lack of data on the contamination of saline water bodies and the modifying effects of salinity on surface water contamination (Williams, 1993). Very little geochemical work has been done on De Hoop Vlei and the sediments have never been investigated geochemically. The water chemistry is characterised by a high degree of spatial and temporal variation and is influenced by a number of different processes.

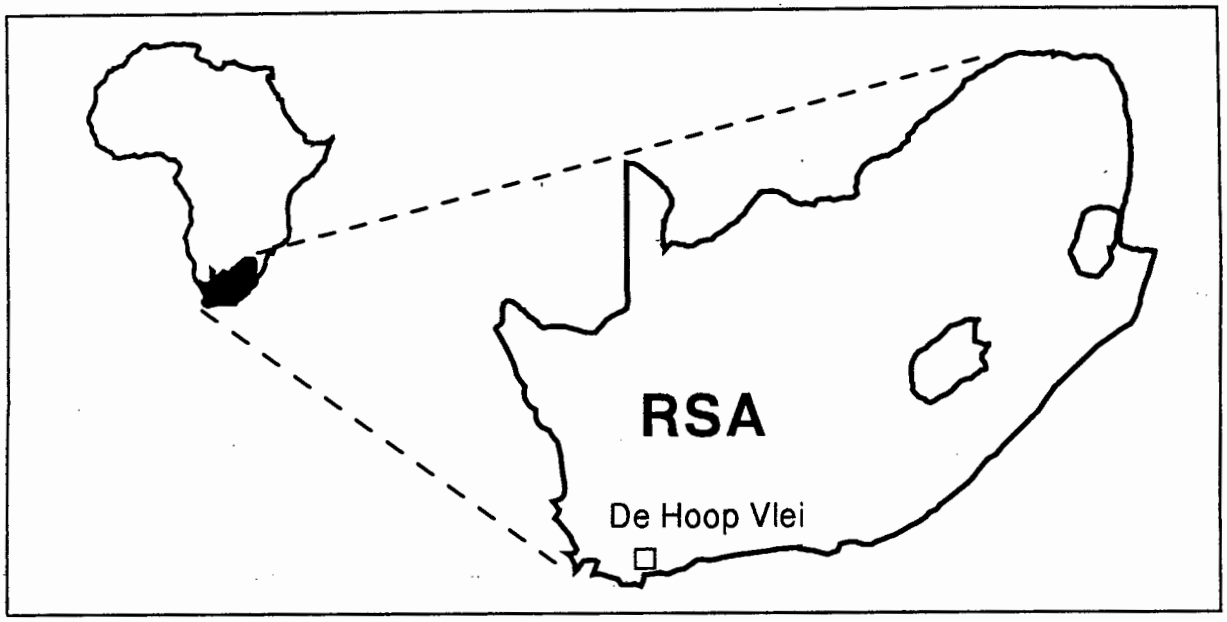

Figure 1.1 The approximate location of De Hoop Vlei within South Africa.

From an environmental point of view the vlei presents an ideal area to study the effects of agricultural practices on water quality. This is because land in almost the entire catchment is intensively cultivated and only a small portion remains in an undisturbed state. Furthermore the endorheic drainage basin with no surface outflows means that anything transported by surface waters from the catchment is likely to accumulate in the water or sediments of the vlei. Such a situation facilitates a study of the behaviour and fate of contaminants.

Furthermore, as a natural system of ecological importance and as an example of a relatively undisturbed ecosystem, it is essential to understand the functioning of the vlei in order to ensure the effective management and continued conservation of this unique system. Understanding the geochemical processes and their influences on water quality is a vital part of understanding the functioning of the whole ecosystem.

1.2 Previous studies in the area

A short review of relevant, previous studies is given below. A number of studies have focused only on bird populations and are therefore not relevant to the focus of the present study. Some earlier studies have considered aspects of the water chemistry and are cited in Coetzee (1986). More recent ones are discussed individually below.

Butcher (1983) focused on hydrological aspects of the vlei and the catchment area with the

main aim of investigating whether land management practices have had an influence on the hydrological processes, particularly with regard to flooding of the vlei. This was achieved through a survey of land use characteristics from historical records and by reference to established techniques for modelling runoff from rainfall data. An additional aim of the study was to document the characteristics of the De Hoop catchment. The conclusion of the study was that, although large differences in run-off may occur in localised areas due to changing land management practices, it was not possible to provide an answer as to whether human impact had changed streamflow to De Hoop Vlei. This was because of the composite characteristics of the catchment.

Coetzee (1986), in a study of zooplankton in the vlei, monitored some aspects of water chemistry at two sites in the vlei. Water levels dropped during the study by 1.1 m and salinity increased from 6.5 g/L to 13.5 g/L. No temperature stratification was measured in the vlei during the study and water was found to be well oxygenated throughout the column except on one occasion during windless conditions. The highest oxygen saturation of 128 percent was attributed to a very high phytoplankton concentration, which was measured at the same time. The pH varied between 7.9 and 9.6 with slightly higher values at night. The lowest pH value recorded coincided with the lowest oxygen saturation of 30 percent. The study found the water to be rich in zooplankton.

Scott and Hamman (1988), in carrying out a fish survey in the vlei, monitored salinity levels at two sites in the vlei over a period of three years. These salinity levels were compared to readings of the water level recorder at the De Hoop homestead for the same period. The results are significant as they give salinity levels at low water levels and states of high evaporative concentration in the southern portion of the lake at times when the continual water monitoring station established by the Department of Water Affairs and Forestry (DWAF) is unable to function because of the low water levels. They also record salinity levels at Tierhoek where the processes controlling salinity differ from those in other parts of the vlei. From the results it is evident that the salinity at De Mond varies inversely with water level. The salinity at Tierhoek, however, remains relatively constant while the pools are isolated from the main water body during dry periods, but increases when the pools are inundated by the main water body. At De Mond, measured salinity varied from 2 g/L to 60 g/L and at Tierhoek, it varied between 0.5 and 2 g/L.

Day (1993) analyzed data on De Hoop Vlei collected by the Department of Water Affairs and Forestry in a comparison between the major ion chemistries of some Namibian and South African saline water bodies. She characterised the different waters in terms of their major ion

chemistry and used the De Hoop data as an example of the effect of evaporative concentration on the water chemistry of a South African coastal lake.

PD Toens and Associates (1994) were contracted to investigate the geohydrology of the De Hoop Nature Reserve with a view to water supply in the reserve, and produced a number of progress reports as a result. As part of their original study they characterised water quality in the area, including the water in De Hoop Vlei and some of the springs that feed the vlei. They have also monitored phosphate and nitrate inputs to the vlei from the catchment area and salinity levels in the vlei. Their findings are discussed in more detail in Chapter 3.

Data on De Hoop Vlei have also been collected by undergraduate students from the Zoology Department at the University of Cape Town during a limnological field trip in 1996. Some of their findings are referred to in Chapter 4 of this study.

1.3 Aims of the study

The aims of this study are to answer certain key questions which have been posed about the De Hoop Vlei system. The central key question is:

- What geochemical factors and processes control the water chemistry of De Hoop Vlei?

Three other key questions which relate to the central one have also been posed. These are:

- To what extent is the water chemistry buffered against changes?

- Is there evidence of agricultural contamination in the vlei or in the waters of the catchment ?

- What is the fate of possible contaminants in the system and would they have the potential to affect the ecology of the vlei ?

The approach of this study has been to focus on an interpretation of the analyses of collected data and to explain the results from a geochemical perspective. Use has also been made of other data in order to examine long-term behaviour of the system. In this way the factors and processes controlling water chemistry in the vlei have been identified in order to answer the central key question. This has also made it possible to draw conclusions about the system and

to answer the other key questions. The final key question is answered using geochemical modelling. In answering these questions this study has attempted to show the importance of the geochemistry of a natural system to its ecology and management as a protected natural environment.

The focus of this study is on the water chemistry, and its purpose is to understand the water chemistry because of its important effect on the ecological functioning of the system. The water chemistry controls productivity of the system and, therefore, has an important effect at the bottom of the food chain (Wetzel, 1983). The sediments are investigated mainly with respect to their role in controlling water chemistry.

In answering the key questions this study is subject to certain limitations. These are mainly a result of the short period of duration of the study combined with the fact that the De Hoop Vlei system undergoes considerable temporal variation. This variation is caused by fluctuations in the water level of the vlei which result in variations in its physical, chemical and biological characteristics. Because data for this study could only be collected over a short period of time, they do not adequately cover these variations and effectively only give a picture of a dynamic system at a particular moment in time. This problem has been overcome to a certain extent by making use of monitoring data collected over much longer periods by DWAF and PD Toens & Associates. These data have assisted in making interpretations about the long-term behaviour of the system. The study has also been subject to analytical limitations. It was originally hoped that an analysis of pesticides in the waters would be undertaken but this was not possible.

Because of the fairly extensive distribution of sampling sites used in this study, it has been possible to effectively address the spatial variation in water chemistry. It is important to understand controls on spatial variation particularly from a monitoring point of view. Most previous data on the water chemistry have not covered the full extent of the spatial variation.

1.4 Description of the study area

The study focused on the De Hoop Vlei itself but the study area included some parts of the catchment. Characteristics of the catchment are obviously important in determining conditions in the vlei. Certain aspects of the vlei and catchment are discussed below and a map of the area is given in Figure 1.2. A more detailed map of the vlei is given in Figure 1.3.

1.4.1 Physiography

The catchment covers an area of approximately 1200 km^2. It is an area of low relief with undulating topography. The maximum altitude in the north west is 355 m above sea level and in the east is 611 m in the Potberg mountains. The entire catchment is close to the coast with the furthest point being 65 km from the sea. It is drained in the west by the Sout River and a number of small tributaries. The Sout River is 141 km long with a low channel gradient throughout its length. The Potberg River, a tributary of the Sout River, drains the catchment from the east. Butcher (1983) found that the catchment had a sluggish response to rainfall and therefore classified it as hydrologically large.

North of the vlei is a line of limestone hills, known as the Duine, which run parallel to the coastline in an east west direction. The hills separate the agricultural land to the north from the De Hoop reserve which includes much of the hills and the plains southwards to the coast. The landscape of the reserve has been identified as high density karst characterised by various types of enclosed depressions, dry valleys and caves (Marker, 1981). The Sout River cuts a gorge through these hills in which the northern part of the vlei is situated.

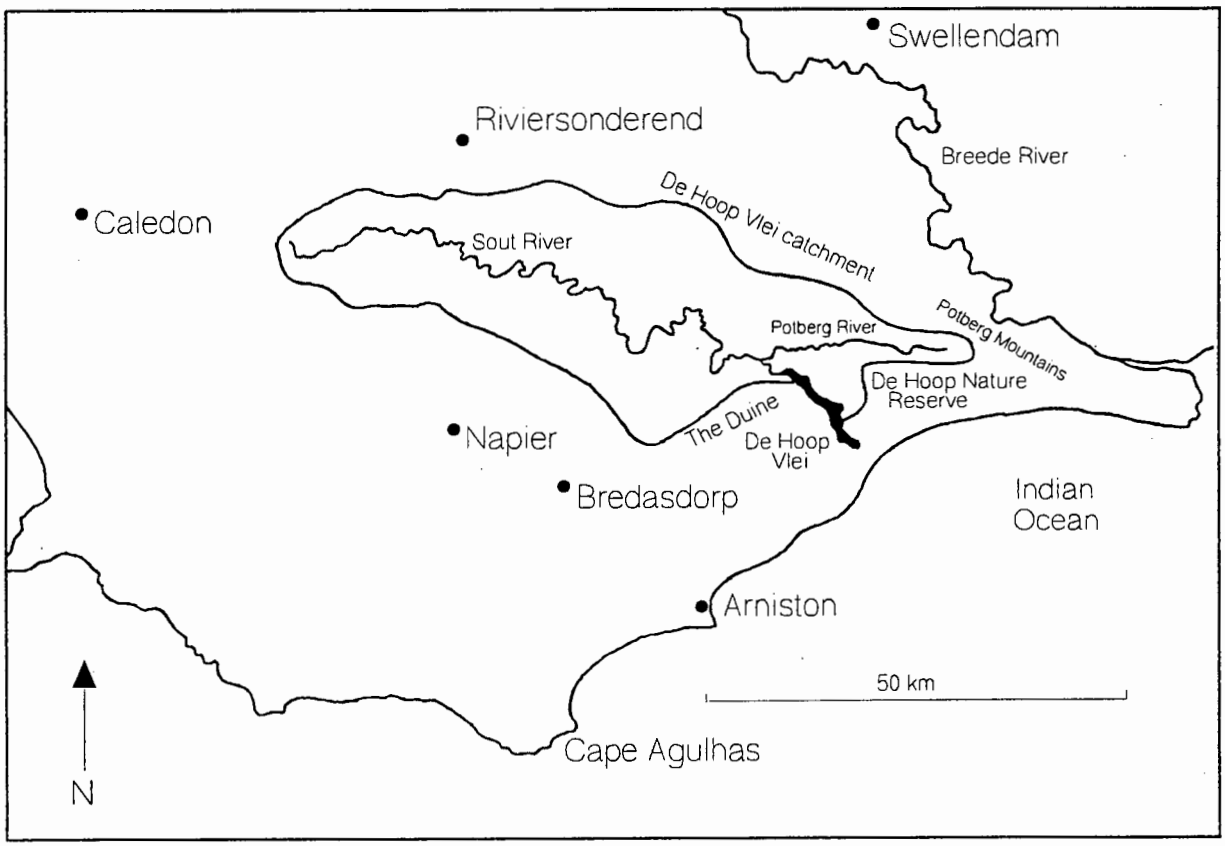

Figure 1.2 Map of the study area showing the De Hoop Vlei catchment and surrounding area.

The De Hoop Vlei extends in a south south-easterly direction from the gorge towards the coast. The vlei has a length of 16 km, an average width of 0.5 km and a surface area of 6.2 km^2. Total capacity of the vlei has been estimated at between 30 and 38 million cubic metres (Butcher, 1983). It is bordered on the eastern side by limestone cliffs which are up to 15 m high. In the northern parts of the vlei springs feed into the vlei from the base of these cliffs with the largest being at Tierhoek. The western bank has a gradual slope with a large area of flat, low-lying land adjacent to it. This land has been inundated in times of flood. The bed of the vlei has a very shallow gradient southwards. The lowest point, at De Mond, is at an elevation of 3.7 m above mean sea level (Butcher, 1983). The vlei is separated from the sea by 2.5 km of mobile sand dunes which run parallel to the coast and are significantly higher in altitude than the vlei.

The vlei is shallow and surface area is large in relation to volume. Water levels do, however, undergo considerable fluctuations depending on rainfall. During this century it has both flooded the western bank and been dried out to varying extents. As the vlei dries out standing water becomes reduced to a pool of decreasing surface area and depth in the south of the vlei at De Mond and to pools of relatively fresh water in the vicinity of Tierhoek. On at least one occasion the entire bed of the vlei, except for the pools at Tierhoek, has been exposed (Butcher, 1983).

1.4.2 Geology and hydrogeology

The geology of the area has been described by PD Toens and Associates (1994a) and a summary of that description is given in this section. The geology consists of tertiary limestones, shales and sandstones. The limestones were deposited in shallow marine and coastal environments on wave-cut platforms which had been cut into the underlying basement rocks. These are the youngest sediments in the area and were deposited during the last 5 million years when the sea encroached to a maximum of 25 km inland from the present coastline. The basement geology comprises sedimentary rocks of the Table Mountain Group, Bokkeveld Group and Uitenhage Group. The Bokkeveld Group shales underlie the limestones in much of the De Hoop Nature Reserve, including parts of the vlei. Sedimentary rocks of the Uitenhage Group outcrop in parts of the Sout River gorge. They are overlain by Bredasdorp Group limestones in the vlei area and are underlain by Bokkeveld shales. Table Mountain sandstones outcrop in the eastern part of the catchment and form the Potberg Mountains. These sandstones constitute an important aquifer and yield good quality water.

The Bokkeveld shales are generally poorly exposed and deeply weathered and typically form

the undulating topography of the catchment north of the Duine. Boreholes within these shales yield high salinity water not fit for drinking or irrigation. This is because downward percolation is slow resulting in a high degree of mineralisation with Na and Mg salts.

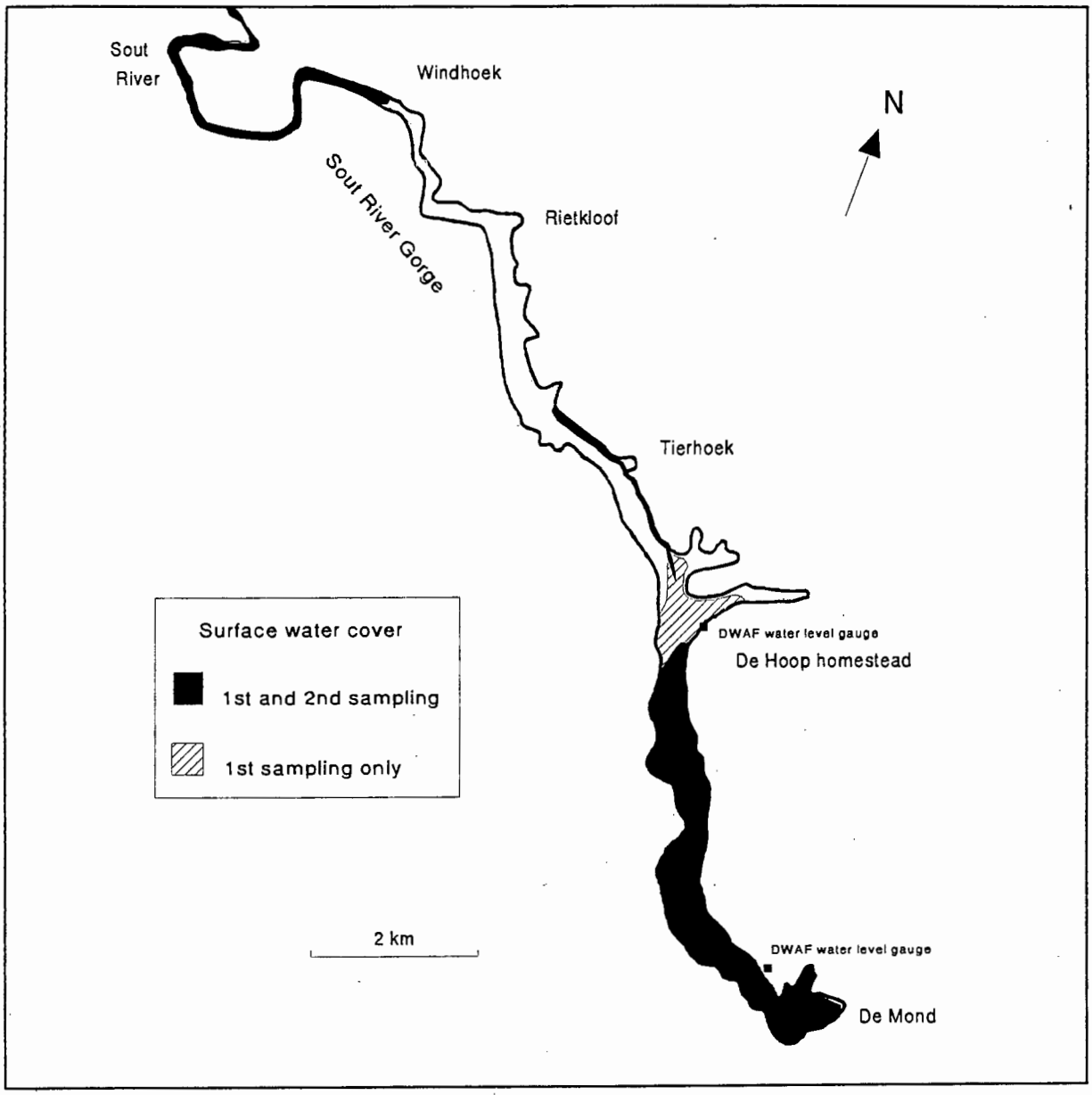

Figure 1.3 Map of the De Hoop Vlei showing approximate surface water coverage during the periods when samples were collected for the study.

Figure 1.4 Taking sediment samples at De Mond in the southern part of De Hoop Vlei. The view is southwards, towards the dunes that separate the vlei from the sea.

Figure 1.5 From Tierhoek looking north with the Tierhoek water body in the foreground and the southern end of the Sout River Gorge and the 'Duine' in the background. The limestone cliffs, which run along the eastern bank of the vlei, are clearly visible.

The Bredasdorp Group is divided into four formations. The De Hoop Vlei Formation comprises shelly limestones and calcarenites with shelly conglomerate packages, and is between 8 and 17 m thick. Carbonate content is greater than 60 percent. It forms the cliffs on the eastern edge of the vlei (Fig. 1.5). Large quantities of good quality groundwater may be found perched on top of the more impermeable basement. Springs, such as the one at Tierhoek draining the limestone hills, issue at the limestone-shale contact. The Wankoe Formation forms the bulk of the group, covering much of the area of the reserve. It is capped at the surface by a calcrete cover. The Strandveld Formation comprises recent unconsolidated calcareous wind blown sand and forms the shifting sands between the De Hoop Vlei and the sea.

1.4.3 Soils

Soil mapping and description work by Smit and Goldswain (1980, cited in Butcher,1983) identifies two main soil types present in the catchment. These, classified according to the soil classification system used in South Africa, belong to the Mispah and Glenrosa soil forms (Soil Classification Working Group, 1991). Both of these forms are characterised by a low degree of weathering and are consequently shallow, with the underlying shales immediately below the A horizon in the case of the Mispah, and contributing to the structure of the B horizon in a partially weathered state in the case of the Glenrosa. These two forms cover 60 - 80 percent of the region. Other soil forms which occur infrequently in the catchment are Shortlands, Swartland and Hutton. Butcher has noted the high potential for erosion in the catchment, given the high erodibility of the dominant soil forms combined with the hilly topography. The disturbance of the natural vegetation through cultivation would also increase the potential for erosion.

1.4.4 Climate

Rainfall occurs predominantly in winter with some occurring throughout the year. The annual average precipitation is approximately 350 mm with the maximum mean monthly rainfall in August and the minimum in December and January. The range in rainfall within the catchment is from 330 to 410 mm per annum.

Mean annual temperature is 16.8 °C with an average summer maximum of 20.5 °C and average winter minimum of 13.2 °C. Windy conditions are very common. The prevailing wind direction is from the south with an average velocity of 35 km/h but winds can exceed 60 km/h.

The Mediterranean climate and windy conditions are conducive to high rates of evaporation.

1.4.5 Ecology

As the vlei is situated in an area which is managed as a protected natural environment, the ecology and its interaction with the geochemistry are important considerations. Here, a brief description of the ecology of both the vlei and the catchment is given. The indigenous vegetation of the area has been described by Acocks (1975, cited in Butcher, 1983). Vegetation of the catchment north of the Duine has been identified as Coastal Rhenosterbosveld. However, very little of the natural vegetation remains as most has been replaced by cultivated lands. The area south of the Duine, which falls within the nature reserve, is Coastal Macchia which grows on limestone-derived soils. One of the purposes of the reserve is the conservation of this vegetation type. Riverine bush occurs on the eastern banks of the vlei.

De Hoop Nature Reserve is well known for its large variety of resident and migrant bird species. Two hundred and fifty nine species have been recorded in the reserve of which 17 are Red Data Book species. The vlei is an important habitat for waders and water birds. Vertebrates of the vlei include the Cape clawless otter and Cape terrapins, which were recorded fairly frequently in the vlei several decades ago but are now seldom seen (Butcher, 1983). Only two fish species occur in the vlei, the indigenous Cape kurper *Sandelia capensis* and the introduced Mozambique tilapia *Oreochromis mossambicus*.

Primary productivity of the De Hoop Vlei was investigated in a study during low water levels (McQuaid, 1996). The flora were dominated by the submerged macrophyte *Potamogeton pectinatus* with scattered beds of *Chara* sp. and *Cladophora* sp. in water uncolonized by *Potamogeton*. Emergent macrophytes such as *Phragmites* and *Scirpus* occur in the northern sections of the vlei, particularly where springs of lower salinity water emerge. The study found that productivity was dominated by *Potamogeton* and that phytoplankton counts and overall phytoplankton productivity were quite low. Zooplankton productivity on the other hand was found by Coetzee (1986) to be high.

1.4.6 Agricultural practices

Agriculture in the catchment consists predominantly of wheat cultivation. Crops grown in rotation are wheat followed by planted pasture which is in turn followed by barley or oats. Use of agrochemicals include fertilizers which usually contain the major nutrients N, P and

K and fungicides to combat rust which is a regular problem in the area. Fertilizers containing Zn have also been used. Examples of commonly used pesticides are Kerb and Glean. Aerial crop spraying is the most widely used method of pesticide application (Butcher, 1983).

1.4.7 Conditions at the time of sampling

Sampling for this study took place during two separate sampling trips, with six weeks between them. The first sampling trip in October 1996 coincided with a period of high rainfall in the study area. This rainfall followed a long dry period of poor rains with no major inflows occurring to the vlei since July 1994 (PD Toens and Associates, 1996). Rainfall started several days before sampling commenced and continued until the last day of sampling. There was little rain between the two sampling trips. Surface water coverage in the vlei during the two sampling periods is shown in Figure 1.3. During the first sampling period surface water coverage increased during the rains. The water level dropped slightly between sampling trips and areas that were covered by the rains during the first sampling in the region of the De Hoop homestead had dried by the second sampling trip. A comparison of surface water coverage in this area is given in the photographs in Figure 1.6. Access to the northern parts of the vlei was not possible during the first sampling trip and surface water coverage was, therefore, not recorded there at that time. During both sampling periods the water level was below the recording gauge at the De Hoop homestead. During the second sampling trip the water level gauge in the De Mond area gave a reading of 1.2 m.

With the low water levels at the time of sampling, an area of exposed vlei bed was present around the perimeter of the vlei. This area was covered in the southern parts, south of the De Hoop homestead region, by a mat of dead plant material.

1.5 Sampling rationale

Sampling stations were chosen to adequately cover the possible spatial variation within the vlei. For this purpose, samples were taken at intervals along the entire length of the vlei. In the region of the De Hoop homestead a transect of three samples across the vlei was also taken in order to investigate variation in this direction. Core samples were taken some distance into the vlei from the water's edge, where possible. This was in order to get samples representative of the bottom sediments of the vlei. Most core samples were taken where standing surface water was present rather than in dry areas. This was done in order to get samples which were currently influenced by interaction with the water column.

(a)

(b)

Figure 1.6 A comparison of the different surface water coverage that occurred at the time of the two sampling trips. These views show the vlei in the region of the De Hoop homestead looking northwards towards the Sout River Gorge. The photograph in (a) was taken on the first sampling trip and that in (b) was taken on the second.

Some water samples were taken from the catchment to give an indication of input waters to the vlei but no sediment samples were taken there and water sampling in the catchment was not done extensively. However, the first sampling in the catchment was done during a period of heavy rains. It therefore maximised the effect of runoff from agricultural fields and some sampling sites were chosen to give any indication of contamination occurring from this. Samples taken during the second sampling trip give a good indication of the baseline condition of input waters to the vlei.

During the second sampling trip some previously sampled sites were re-sampled in order to get an indication of changes in the water chemistry that had occurred between trips and to be able to compare results between the two sets of samples.

The details of sampling procedures for water and sediment samples will be covered in chapters 3 and 4 respectively. The next chapter presents a review of the literature covering the geochemistry of shallow saline lakes. This is followed by a chapter on the aqueous geochemistry and one on the geochemistry of the sediments of De Hoop Vlei. These chapters present and discuss the results of the present study. A final chapter answers the key questions which were posed at the beginning of the study.

Chapter 2 The geochemistry of shallow, saline lakes - a literature review

2.1 Introduction

Saline lakes occur world-wide in areas where environmental conditions are conducive to the accumulation of salts in closed drainage basins. Their global distribution and the extent of their occurrence makes them important in a consideration of surface waters. The total volume of inland saline water on the earth is only slightly less than the volume of surface fresh water (Comin and Williams, 1994). Williams (1994) has stressed the importance of researching saline lakes in order to effectively manage their conservation. In South Africa, most saline water bodies occur as ephemeral salt pans. Some coastal saline lakes of estuarine origin, such as De Hoop Vlei, also occur.

The purpose of this literature review is to detail the geochemical processes that have been identified in previous studies to have a controlling influence on the water chemistry in saline lakes. The emphasis of this literature review is on shallow, polymictic saline lakes because De Hoop Vlei may be classified as such. Therefore, although the concept of water stratification is briefly covered, details of its influence on water chemistry are not.

2.2 Classification of saline lakes

The most important factor in the classification of saline lakes is the level of salinity. A classification of different water bodies according to salinity has been established and is now widely accepted (Hammer, 1986). In terms of this classification all waters with a salinity of greater than 3 g/L are classified as saline. Waters with salinity of less than 0.5 g/L are classified as fresh while those between 0.5 and 3 g/L are sub-saline. Saline waters are further subdivided into three categories: hyposaline < 20 g/L, mesosaline 20 - 50 g/L, and hypersaline >50 g/L. These are limnological classifications and the ranges of salinities are based on the likely occurrence of different species at different levels of salinity.

Saline lakes are also classified according to their association with marine waters. In this regard, athalassic saline lakes are differentiated from marine saline lakes. Athalassic lakes are defined as lakes which have had no connection to the sea in geologically recent times, or which have been evaporated to dryness after having been flooded by marine waters and subsequently re-flooded by non-marine waters (Hammer, 1986). The important differentiating factor between athalassic and marine saline lakes is, therefore, the present supply of water to

the lakes. Athalassic coastal lakes receive water from the inland catchment areas by way of rivers or ground water seepage while marine coastal lakes receive some input directly from sea water via ground water seepage (Mackenzie *et al.*, 1995). The athalassic nature of a lake is irrespective of its position relative to the coastline (Hammer, 1986). The limnological significance of the classification of a lake as athalassic is that the fauna and flora of the lake are not directly derived from marine biota.

Saline lakes are also distinguished from playas or pans. Saline lakes are perennial and although they do dry up occasionally, their definition is dependent on the persistence of surface water for many years. Playas are ephemeral and are found in regions where surface runoff is insufficient for the persistence of surface water to occur (Shaw and Thomas, 1989).

2.3 Non-chemical characteristics of saline lakes

2.3.1 Environmental factors controlling occurrence

Certain climatic and geological conditions are necessary for the formation and persistence of saline lakes. These conditions are that evaporation exceeds precipitation, that the drainage basin is hydrologically closed and that a supply of soluble salts is available for accumulation. (Wetzel, 1983; Hammer, 1986). Permanent saline lakes typically occur in semi-arid or sub-humid regions. In arid regions the supply of precipitation for runoff is too little to result in permanent water bodies and in humid regions runoff is too great to allow for endorheic or closed drainage basins which lack surface outflow. The most important aspects of climate in relation to saline lakes are evaporation and precipitation rates, humidity, insolation, temperature and winds (Hammer, 1986).

Prevention of runoff reaching the sea is brought about by a combination of both climatic and geographical factors. The combination of geological barriers with a climate in which evaporation exceeds precipitation prevents water depth from reaching levels which would permit surface outflow (Hammer, 1986). Different geological origins of lake basins have been identified throughout the world. The major ones include tectonic, volcanic, glacial and wind action/ deflation (Hammer, 1986). Other less common origins include coastal processes as in the case of De Hoop Vlei.

2.3.2 Physical processes

2.3.2.1 Stratification of the water column

Three types of saline lakes have been identified by Hammer (1986) in terms of the stratification of the water column. The first are polymictic lakes where no stratification occurs. The water column is mixed to the bottom either continually or on a daily basis. Such lakes, therefore, have a permanent aerobic environment above their sediments. This is a common condition of many saline lakes as they are frequently shallow and occur in areas of high wind.

The second type are thermally stratified lakes. This is a common condition for lakes which are deeper than about 10 metres. Stratification is the result of the heating of surface waters by solar radiation at warmer times of the year. The surface waters become less dense and are separated from the underlying water by a thermocline at a certain depth. Stratification remains in place for a period of time but then mixing of the entire water column takes place as a result of seasonal changes in temperature and solar radiation.

The distinctive feature of the third type, meromictic lakes, is that part of the lake fails to circulate over the long term with the rest of the lake. The underlying portion that does not mix is termed the monimolimnion. The mixolimnion is the upper portion which mixes freely. The two portions are separated by the chemocline where salinity and therefore density increases with depth and prevents mixing. The result is an upper layer of less dense, less saline water overlying a monimolimnion of more saline, denser water. A method for calculating the chemical stability of stratification in meromictic lakes has been developed (Idso, 1973).

Stratification has an important influence on the chemistry of the water column largely by influencing redox conditions. A build-up of the concentrations of a number of elements is associated with reducing conditions - for example the build up of dissolved H_2S in the monimolimnion (Last, 1993). It also has an important influence on chemical sedimentation since the degree of saturation differs between the different layers in the water column.

2.3.2.2 Sedimentary processes

The sediments of salt lakes may be divided into different fractions. Certain fractions are dominated by physical processes and consist predominantly of siliciclastic material. Other

fractions are dominated by chemical processes. Last and Schweyen (1983) have identified four different fractions in the sediments of saline lakes. These are very soluble evaporites, sparingly soluble precipitates, organic detritus and clastic inorganic material. The first two fractions are the result of chemical processes and are discussed in section 2.4.3. The physical sedimentary processes that affect clastic sediments are briefly reviewed here.

Clastic inorganic material is deposited in lake sediments by three processes, namely surface runoff from the catchment, shoreline erosion and wind. Due to the transport processes the sediments are largely fine-grained (Shaw and Thomas, 1989). The sorting of sediments by particle size occurs in lakes due to wave action and consequent shoreline erosion. Finer grained fractions are transported away from the shoreline by wave action because they are held in suspension and are deposited in the deeper basins of the lake. Flocculation of clay-sized material also plays an important role in the depositional process. Common clay minerals in the sediments of saline lakes are kaolinite, montmorillonite and illite (Hammer, 1986).

A physico-chemical process that may influence the sedimentation of clastic clay minerals is the differential flocculation of these minerals (Burton, 1976). This occurs because different clay minerals show different degrees of stability in their tendency to coagulate as a result of increasing salinity. Burton cites a case where kaolinite and illite were separated in an estuary with kaolinite flocculating first and dominating the upper parts, and decreasing in concentration down river while illite showed the opposite trend. Cases of montmorillonite occurring lower in an estuary than kaolinite and illite because of differential flocculation have also been recorded (Burton, 1976).

Saline basins which are dominated by inputs of surface flow rather than groundwater flow usually have clastic material as the dominant sediment fraction with a high clay content (Shaw and Thomas, 1989). The layering of clastic and chemical sediments is common in saline lakes. This occurs because thin layers of mud are deposited infrequently during storms. These thin layers divide the chemical sediments which are deposited continually over long periods.

2.4 Chemical characteristics

2.4.1 Origins of salts

Hammer (1986) identifies three possible origins of the salts in saline lakes. These are earlier marine deposits, the soluble salt content of soils and rocks of the catchment area, and salts

transported from the sea via the atmosphere. Although there is disagreement over the importance of atmospheric salt supply to inland saline lakes, it is agreed that this contribution may be important for coastal lakes (Hammer, 1986). Mulcahy, in an Australian study (cited in Hammer, 1986), measured 100 kg/ha per annum of chloride in rainfall and dry fallout close to the coast. It was also found that the amount of salts decreased rapidly with distance from the coast.

The chemical composition of inflow waters is the most important factor determining the composition of evolved saline waters. Gibbs (1970) has identified surface waters of the world as being controlled by three major mechanisms: atmospheric precipitation, rock dominance and evaporation. He showed that waters dominated by each of these factors will plot in different areas of a graph of Na/(Na + Ca) versus total dissolved solids (TDS).

2.4.2 Evolution of saline lake water

Athalassic saline lakes are brought about by the accumulation of salts in a hydrologically closed basin. The input waters are usually dilute in comparison to the lake waters and accumulation takes place gradually as a result of the combination of inputs of salts and evaporation. As the salt load increases in the lake, geochemical processes occur which cause a change in the composition of the waters. Quantitative models have been developed to explain the way that the chemistry of lake waters change as a result of the accumulation of salts.

An important forerunner of such models was initially developed by Garrels and Mackenzie (1967, cited in Drever, 1988) and later generalised by Hardie and Eugster (1970, cited in Drever, 1988). The initial model, developed for a particular water composition, showed that the chemistry of several natural saline lakes in the western United States could be explained by evaporation of dilute spring water which would bring about the precipitation of a sequence of different minerals. The Hardie-Eugster model generalized the calculation procedure of the initial model to cover a wide range of starting compositions for the water to be evaporated.

The model is based on the calculation of the saturation index of different minerals. Evaporation of water results in an increase in the salt load and the solution becoming saturated with respect to a particular mineral. Such a mineral is then allowed to precipitate until the water is depleted with respect to one of the components of that mineral. Further evaporation and increased salinity then results in another mineral becoming saturated and being allowed to precipitate. In the original model the sequence of precipitation was calcite

($CaCO_3$) resulting in Ca depletion followed by sepiolite ($Mg_4Si_6O_{15}(OH)_2.6H_2O$) resulting in Mg depletion and then amorphous silica precipitation.

An important concept in the Hardie-Eugster model is that of the chemical divide. The essence of this concept is that when two ions are involved in the precipitation of a salt during evaporation, the ion present in greater relative concentration in solution will increase in concentration while the concentration of the other will become very small. The Hardie-Eugster model interprets the chemistry of waters undergoing evaporation in terms of a succession of chemical divides. This is illustrated in Figure 2.1.

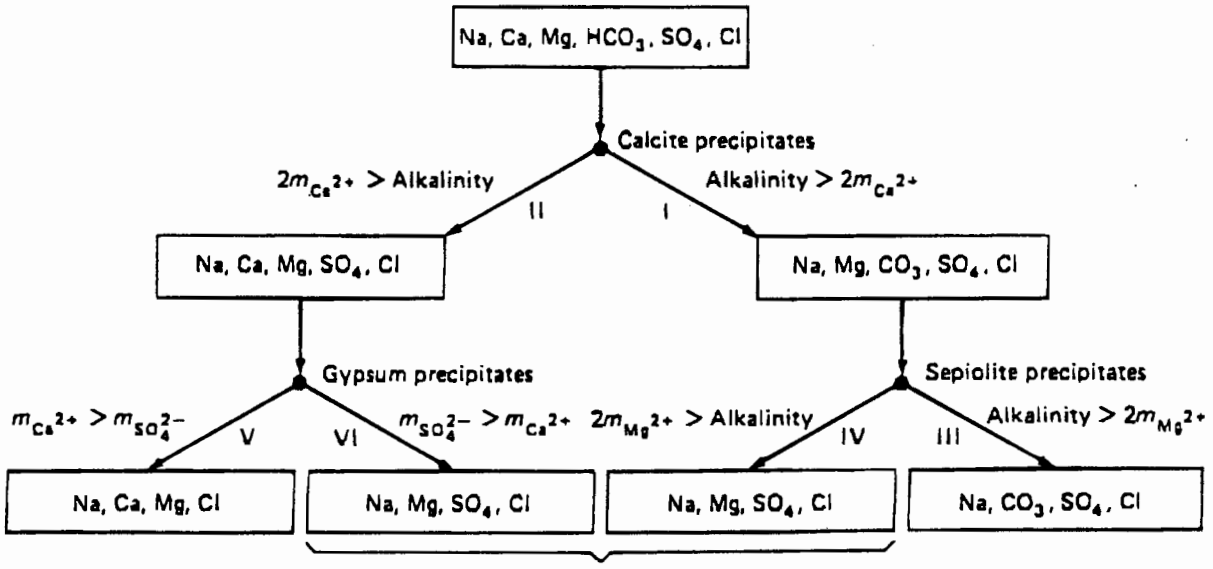

Figure 2.1 A schematic diagram of the Hardie-Eugster model showing the evolution of saline brines along different possible paths (modified from Drever, 1988).

The first mineral to precipitate in the model and in almost all natural waters (Drever, 1988) is calcite. Calcite precipitation brings about the first chemical divide. The subsequent path followed by a water depends on which of Ca or alkalinity has the highest concentration (in equivalents). If alkalinity has the higher concentration, all Ca will depleted and the water will follow path I in Figure 2.1 and tend towards an alkaline carbonate brine. However, if Ca has the higher concentration, all alkalinity will be depleted and the water will follow path II and tend towards a nearly neutral sulphate or chloride brine. Following path I, the next mineral to precipitate in the model is sepiolite. Here the chemical divide is dependent on which of Mg or alkalinity has the higher concentration in equivalents, following calcite precipitation. The

water can either evolve into an alkaline carbonate brine along path III if alkalinity is higher, or a carbonate-free, sulphate or chloride brine on path IV if Mg is the higher.

On path II gypsum ($CaSO_4.2H_2O$) is the next mineral to precipitate. If Ca concentration is greater than sulphate, path V is followed to form a brine which has chlorides of Na, Mg and Ca as the major solutes. If sulphate concentration is the greater, a brine with chloride and sulphate as the major anions and Na and Mg as the major cations will be formed. The Hardie-Eugster model shows that the composition of the final brine is determined by the composition of the dilute water from which the brine was derived. It also shows that the brine should be chemically simple with relatively few ions as major components because of the depletion of other constituents by precipitation.

Renaut (1990) found that the precipitation of carbonates constituted a major chemical divide in saline lakes in British Columbia, Canada. This chemical divide produced two dominant types of brine in the area, a highly alkaline brine poor in Ca and Mg with Na-CO_3-(SO_4)-Cl composition and a more neutral brine poor in carbonate with Mg-Na-SO_4 composition.

The original Hardie Eugster model is an oversimplification of processes that actually occur in saline lakes. Drever (1988) discusses a number of modifications to the model which include other processes which can be important in the evolution of saline lake waters.

The first modification is the precipitation of other Mg minerals instead of sepiolite. Drever (1988) states that the most common Mg-containing phases to be formed in nature appear to be Mg-rich smectite, dolomite or high Mg calcite. Drever further states that, in terms of the chemical divide effect on brine evolution, it makes little difference if Mg is removed as a silicate or as a carbonate. It does, however, make a difference if dolomitization occurs in the absence of excess alkalinity:

$$2\ CaCO_3 + Mg^{2+} \rightleftharpoons CaMg(CO_3)_2 + Ca^{2+}$$

In such a case Ca either builds up in solution or precipitates as gypsum, influencing the end result of brine evolution.

A factor which affects sulphate concentrations during the evolution of saline waters is the reduction of sulphate to sulphide species. Sulphate reduction can be represented by the equation

$$8SO_4^{2-} + 2Fe_2O_3 + 15(C) + 7H_2O \rightleftharpoons 4FeS_2 + 14HCO_3^- + CO_3^{2-}$$

where (C) represents organic carbon and Fe_2O_3 represents the reactive iron minerals in the sediments, with which the water is in contact. The reduction of sulphate is responsible for lowering the sulphate concentration in many saline lake waters. It is also responsible for the low concentrations of sulphate minerals which occur in many saline lake deposits.

Ion exchange and adsorption reactions take place between dissolved components of saline lake waters and the lake sediments, providing a further mechanism which modifies the water chemistry. Adsorption on solid surfaces can affect neutral species such as H_4SiO_4 as well as the sulphate anion. The ion most affected by ion exchange reactions is potassium (Drever, 1988). Potassium salts are not precipitated except at very high concentrations but K^+ is usually depleted in saline waters relative to Na as a result of its preferential adsorption on exchange sites, particularly in the interlayers of silicate clay minerals .

The final process identified by Drever as modifying brine evolution is cyclic wetting and drying which brings about the differential dissolution of efflorescent crusts. This results from the complete evaporation of a water and deposition of solutes during a dry period followed by partial re-solution of these solutes during a wet period. All solutes are deposited following evaporation but during re-solution the rate at which some less soluble compounds dissolve may prevent their dissolution. The evaporation-solution cycle, therefore, enriches the resultant brine in highly soluble salts but depletes it in salts which have a slow rate of dissolution. This process was found to be the major process controlling water chemistry in Teels Marsh, Nevada (Smith and Drever, 1976) and in the Salt Lake (Tuz Gölü) basin in Turkey (Camur and Mutlu, 1996).

In saline lakes of the Basotu district in Kenya, brine evolution was found to be the result of a combination of all these biogeochemical processes identified above (Kilham and Cloke, 1990). A rapid pathway of brine evolution was also identified. The authors argue that this occurs when mixing events cause H_2S to be suddenly lost to the atmosphere. The loss of sulphate, which is reduced to H_2S, is combined with a gain in permanent alkalinity.

During brine evolution different solutes are affected to varying extents by the chemical processes which operate in saline waters. Five different patterns of behaviour have been identified by Eugster and Jones (1979) and are illustrated in Figure 2.2. A type I solute is termed conservative and its concentration increases linearly with increasing salinity of the water. The total amount of such a solute remains in solution at all stages of evaporative

concentration. Near perfect conservative behaviour is usually shown by Na and Cl. The chloride concentration is frequently plotted against other solute concentrations to indicate departure from conservative behaviour.

Type II solutes contain a cation and anion which co-precipitate, with type IIb having the limiting concentration in terms of the mineral being precipitated. Because of the effect of the chemical divide, the concentration of type IIb will become very small while the concentration of IIa increases but not as rapidly as type I solutes. Alkalinity and Ca show type II behaviour during the precipitation of $CaCO_3$. A type III solute is removed from solution gradually by a combination of mechanisms. The removal of carbonates by degassing and precipitation in Lake Magadi, Kenya is an example of type III behaviour (Hammer, 1986). Solutes follow a type IV trend where the removal mechanism is most prominent in the middle part of the concentration range and is not strongly concentration dependent. Such removal mechanisms include ion exchange, surface adsorption and biogenic reduction and commonly control the concentrations of K^+ and SO_4^- in saline waters. Uncharged solutes such as SiO_2 show type V behaviour by increasing concentration to saturation and then remaining constant, in equilibrium with a solid phase.

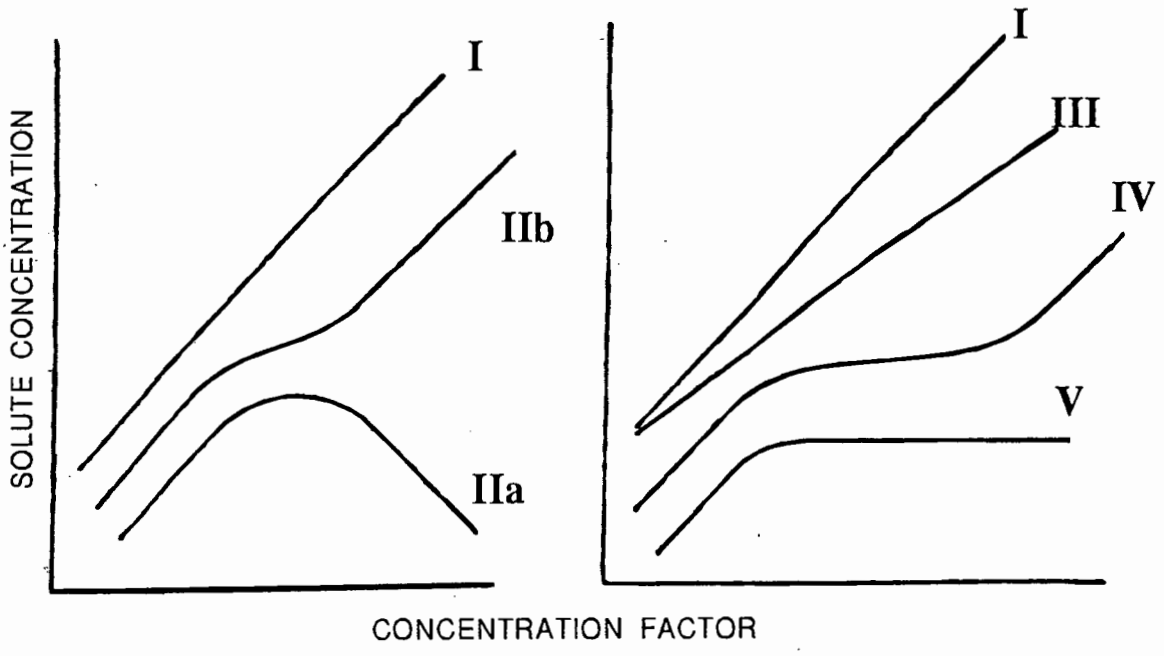

Figure 2.2 Schematic plots of the effect of increasing salinity on the concentrations of different solute types (adapted from Hammer, 1986).

According to Hammer (1986) the order of decreasing conservative behaviour in the major cations is Na, K, Mg, Ca. Calcium and Mg are removed predominantly in saline lakes by precipitation involving carbonates while K is removed by sorption on clay minerals. Wetzel (1983) classifies solutes as conservative and dynamic according to biological influence on their concentrations. Conservative ions undergo minor changes in their concentrations from biotic utilisation and biotically mediated changes in the environment. These include Mg, Na, K and Cl. The concentration of dynamic solutes is influenced strongly by metabolism. Such solutes include Ca, SO_4, Fe and Si. Many authors have investigated the behaviour of different solutes during evaporative concentration by plotting their concentrations against the chloride concentration (Drever, 1988; Renaut, 1990; Kilham and Cloke, 1990; Day, 1993).

In summary, a total of five geochemical processes affect water chemistry in closed basins during brine evolution. The chemical fractionation that takes place between dilute inflow and the concentrated brines is accounted for by mineral precipitation, selective dissolution of efflorescent crusts and sediment coatings, sorption on active surfaces, degassing and redox reactions (Hammer, 1986).

2.4.3 Chemical precipitation and sediment chemistry

Significant precipitation often occurs from the water column of saline lakes (Hammer, 1986). In this way elements are transferred from an aqueous phase to a solid phase and are incorporated into the sediments. The concentration of certain solutes in the water is, therefore, controlled by equilibrium with solid phases. Other elements are influenced by other chemical processes which take place in the sediments. A consideration of the chemistry of the sediments of saline lakes is, therefore, important and is discussed in this section.

2.4.3.1 Mineralogy of chemical sediments

Eugster (1980) states that alkaline earth carbonates are by far the most abundant precipitates in most closed basins. Carbonate minerals were found to be the dominant authigenic minerals in the majority of saline lake basins investigated by Renaut (1990) in British Columbia, Canada.

The dissolved Mg to Ca ratio in the lake water is important in determining the type of carbonate minerals precipitated. Hammer (1986) states that aragonite ($CaCO_3$) forms in preference to calcite where the Mg to Ca ratio exceeds 14. He further states that a higher Mg/Ca ratio (greater than 149) gives rise to Mg-dominated precipitates of magnesite ($MgCO_3$),

huntite ($Mg_3Ca(CO_3)_4$) and dolomite ($CaMg(CO_3)_2$). Observations by Warren (1990) have also suggested that the precipitation of the more Mg-rich carbonate phases is favoured by high salinities as well as greatly elevated Mg/Ca ratios. Dolomite precipitation is also favoured by high carbonate alkalinity and low sulphate concentration (Last, 1992). Renaut (1990) found that precipitated carbonate sediments in the saline lakes of the Cariboo Plateau, Canada included extensive magnesite and hydromagnesite ($Mg_5(CO_3)_4(OH)_2.4H_2O$) deposits and several occurrences of protodolomite.

The chemical sediments of saline lakes may be of authigenic or endogenic origin. Endogenic minerals are those originating from processes occurring within the water column. Authigenic minerals are those originating from processes occurring within the sediments once deposited. Halite, gypsum, calcite and aragonite were identified as being endogenic minerals in the Salt Lake Basin in Turkey (Camur and Mutlu, 1996). Magnesite and huntite were identified in this basin as mostly early diagenetic minerals that were formed by the transformation of dolomite in the presence of pore fluids with a high Mg to Ca ratio. In the Persian sabkhas, gypsum precipitation increases the Mg to Ca ratio and, when it exceeds about six, aragonite in the sediment is converted to dolomite (Drever, 1988).

Carbonate precipitation may occur inorganically or biologically. Algal mounds or bioherms are common in many saline lakes and are important contributors to the carbonate rock record (Eugster, 1980). In a study of two saline lakes in Victoria, Australia, it was found that dolomite, hydromagnesite and magnesite were derived by inorganic precipitation in the water column or at the sediment-water interface whereas calcite was biologically precipitated as ostracod valves (Last and De Deckker, 1990).

Gypsum occurs more commonly in environments not continually covered by surface waters. Hammer (1986) states that the bottom sediments below the littoral usually contain small amounts of gypsum compared to aragonite and calcite. This is widely recognised as being due to the reduction of sulphate to sulphides under anaerobic conditions in the sediments. Gypsum is a common precipitate, together with calcium carbonate, that forms during evaporative concentration of marine lake waters (Mackenzie *et al.*, 1995). When sea water is concentrated precipitation of gypsum occurs when 80 % of water has evaporated and all carbonate has been precipitated (Drever, 1988). Camur and Mutlu (1996) found that gypsum was a major constituent of the sediments of the Salt Lake Basin in Turkey where it occurred together with dolomite, huntite and magnesite.

Different zones within saline lakes have been identified as different depositional environments

(Shaw and Thomas, 1989). The types of minerals that precipitate differ from zone to zone. Carbonate minerals dominate in the bottom sediments which are usually covered with water and where concentrations do not reach as high as elsewhere. Hammer (1986) states that lakes which never desiccate and with moderate seasonal salinity variations have sediments which consist of organic rich muds containing FeS, aragonite and calcite. Surrounding areas such as mud flats are subject to desiccation during low water levels. In areas where complete desiccation occurs, high brine concentrations result and evaporite minerals precipitate. The most common salts found in modern saline lake deposits are halite (NaCl), gypsum ($CaSO_4.2H_2O$), mirabilite ($Na_2SO_4.10H_2O$), thenardite (Na_2SO_4), epsomite ($MgSO_4.7H_2O$), and trona ($NaHCO_3.Na_2CO_3.2H_2O$) (Lowenstein and Hardie, 1985).

2.4.3.2 Elemental composition and chemical processes in sediments

Geochemical processes in saline lakes result in a certain distribution of elements within the lake sediments. Clastic deposition and precipitation account for much of the observed elemental composition of sediments. Mason and Moore (1982) have described the fate of the major elements during sedimentation as follows. Silica concentrates largely in the resistate sediments and alumina in the hydrolysates (essentially the clay minerals). Calcium and magnesium concentrate in the carbonates. Iron and manganese are associated with the oxidates. Most sodium remains in solution or, under highly concentrated conditions, precipitates as evaporite minerals, particularly halite. Potassium is adsorbed by clay minerals.

Additional processes operate in the sediments and influence particularly the distribution of minor and trace elements. Redox conditions in the sediments are of particular importance in this regard (Wetzel, 1983). The redox status of sediments is dependent on oxygen penetration into them which is in turn governed by the rate of oxygen supply to the sediment surface and by the oxygen demand of the sediments. When sediments are overlain by oxygenated water, an oxidised zone can develop at the sediment surface (Wetzel, 1983).

The transfer of a number of elements between the sediments and the water column is greatly influenced by the presence of an oxidised microlayer at the sediment water interface (Wetzel, 1983). The oxidised layer forms an efficient trap for Fe, Mn and P. The mechanism for this has been described by Wetzel (1983) and Hamilton-Taylor and Davison (1995). The solubilities of both Fe and Mn are greatly enhanced under reduced conditions. Dissolved Fe and Mn in the interstitial waters are precipitated when they reach the oxidised zone at the sediment surface. The Fe and Mn oxide precipitates are important scavenging or carrier phases for the labile trace element fraction in aquatic environments. Where they are

precipitated they remove dissolved trace elements and prevent their transfer across the sediment water interface. Hamilton-Taylor and Davison (1995) state that, from available evidence, it appears that Fe oxides have the greatest affinity for As and Cu whereas Mn oxides have a greater affinity for Ba, Co, Zn and Ni. Aston and Chester (1976) state that Mn, Cu, Sc, Zr, and Mo are enriched in anoxic sediments while other trace metals have similar concentration in both oxidising and anoxic sediments.

A reduced environment in the sediments also affects the pH and a difference between the pH of interstitial waters and lake waters often occurs as a result. Mackenzie *et al.* (1995) have demonstrated a sharp decrease with depth near the sediment surface in marine saline lakes. This was due to the presence of CO_2 and H_2S produced as a result of oxidation of organic matter through bacterially mediated sulphate reduction. They also showed that dissolved inorganic carbon is progressively added to the pore water as labile organic carbon is consumed.

2.4.4 The chemical composition of saline lake waters

The above discussion on the evolution of saline lake waters and the interaction between waters and sediments has demonstrated the variety of processes which affect water chemistry of saline lakes. Certain aspects of the resultant water chemistry are discussed below.

The compositional variability of continental brines is one of their characteristics (Eugster, 1980). The factors controlling the type of brine which is produced have been discussed above. The most important of these in terms of brine type is the composition of influent waters. Hammer (1986) classifies three major types of saline lake water based on the dominant anion. The most common are those in which chloride is dominant. Carbonate-dominated lakes, the second major type, are usually in the lower end of the salinity range. The third type are sulphate-dominated. Hammer distinguishes subtypes of these, of which chloride-sulphate, chloride-carbonate and sulphate-chloride are the most common. Of the three major cation types (Na, Mg, Ca), Na is the most common. Five major types of saline lake waters have been distinguished by Eugster (1980). These are Na-CO_3-Cl; Na-CO_3-SO_4-Cl; Na-SO_4-Cl; Na-Mg-SO_4-Cl and Ca-Mg-Na-Cl.

The pH of most saline lakes is above 7 and values as high as 11 occur in some lakes (Hammer, 1986). The pH is affected by carbonate precipitation which commonly occurs. Doner and Lynn (1989) have shown that for waters in equilibrium with calcite the pH increases with a decrease in Ca^{2+} ion activity at a fixed partial pressure of CO_2. The pH is

therefore high in waters in which Ca has been depleted to a large extent through the precipitation of calcite. The dissociation of carbonic acid, which controls the pH of many natural waters, is affected by salinity in that the activity coefficient of CO_3 ions decreases sharply with increasing ionic strength (Hammer, 1986).

Eugster (1980) states that one of the most important mechanisms by which the pH of alkaline waters rises during evaporative concentration is the degassing of CO_2 in response to equilibration with respect to atmosphere and temperature changes. This leads to a decrease in the total carbonate species while the carbonate alkalinity remains constant:

$$2HCO_3^- \rightarrow CO_3^{2-} + CO_2\uparrow + H_2O$$

The pH of lakes is also influenced by biological activity in the water. Photosynthesis removes CO_2 from the water column and therefore causes an increase in pH (Wetzel, 1983).

Oxygen saturation in lake waters is strongly influenced by water stratification. Low levels of oxygen are common in the monimolimnion of meromictic lakes (Hammer, 1986). Mixing by wind is an important mechanism for maintaining high O_2 levels in the entire water column of shallow lakes and the upper portion of stratified lakes (Hammer, 1986). Last (1993) found that high oxygen saturation occurred in the upper 2-3 m of the water column of a stratified saline lake and attributed this to mixing by wind and to photosynthetic activity. Salinity affects the absolute value of oxygen concentration in saline lakes because it reduces the solubility of O_2 in the water (Drever, 1988).

2.4.5 Nutrient dynamics in saline lakes

The nutrient status of lakes is fundamental to the functioning of lake ecosystems. Nutrient dynamics in aqueous systems is a broad subject and only a brief discussion of the basic principles is given in this review. The cycling of nutrients through various pools in the lake environment controls the long-and short-term productivity of the system (Lijklema, 1994). An important pool of nutrients, particularly of P and N, occurs in lake sediments and a variety of biological, physical, chemical and mechanical processes act to cycle these nutrients between the sediments and the water column of lakes.

The nitrogen cycle in lake environments consists of six different processes which determine the amount of biologically available N in the system at any given time (Wetzel, 1983). These are fixation - the reduction of N_2 to organic N; immobilisation - incorporation of organic N

into cell biomass; mineralisation - decomposition of organically bound N to NH_4^+; nitrification - oxidation of NH_4^+ to NO_3^-; denitrification - reduction of NO_3^- to N_2O and N_2; and dissimilatory reduction - reduction of NO_3^- to NH_4^+.

Phosphorus is likely to be the nutrient most limiting to phytoplankton growth in saline lakes although high concentrations occur in some saline lakes (Hammer, 1986). Interactions between the sediments and the water column are important in controlling the phosphorus concentration in lake waters. Sediments can serve as both a sink and source of phosphorus. Liss (1976) states that, in studies on estuarine sediments, phosphorus has been found to be buffered in the water column due to exchanges with the sediments. In these studies removal of P was successfully described using the Freundlich isotherm. Liss also discusses the two-stage uptake theory of P in sediments. This involves a rapid initial stage in which P is adsorbed onto the sediment surface, followed by a slower reaction in which P is incorporated into the structure of the solid phase. Clavero *et al.* (1990) found that P removal by sediments followed a kinetics indicative of P saturation of the sediments.

Wetzel (1983) stresses the importance of the redox status of the sediment-water interface in regulating P transfer between sediments and the water column. An oxidised microzone at the interface forms an efficient trap for P and significantly reduces its movement from the sediments into the water column.

The P concentration in lakes can be used as a measure of their trophic status. Lewis *et al.* (1984) used the following levels for classification of trophic status: oligotrophic (<10); mesotrophic (10 - 20); and eutrophic (> 20 µg/L P).

Silica is essential for the growth of diatoms and some other algal groups, being an integral component in their frustules (Hammer, 1986). They can, therefore, remove large quantities from solution and as a result evaporative concentration does not appreciably raise the silica concentrations of saline lakes above that of inflow. In alkaline brines, however, silica concentrations eventually increase due to polymerization of H_4SiO_4 at high pH (Eugster, 1980).

2.5 Human impacts on the water chemistry of saline lakes

Although many salt lakes world-wide are being negatively impacted upon by human activities, they have not attracted much attention from a conservation point of view (Williams, 1993). A number of authors have drawn attention to their value (Hammer, 1986; Williams, 1993).

An important ecological value of many salt lakes is their role as feeding refuge and breeding sites for many migratory and nomadic bird species. Changes in the water chemistry are likely to affect this ecological function, as has already occurred in the Aral Sea and a number of other saline lakes (Williams, 1993). They are also likely to affect other values and uses of salt lakes. Williams (1993) has reviewed the literature on the impacts of human activities on salt lakes. Those impacts which directly affect the water chemistry are discussed below.

The biggest human induced impact on salt lakes has been the diversion of inflows with a consequent drop in water level and increase in salinity. This has been noted in a number of salt lakes throughout the world (Williams, 1993; Aladin, 1993; Williams, 1996). Inflowing waters are usually diverted for irrigation purposes but may also be used for supply to urban areas (eg. Mono Lake, USA). Other related changes in the catchments of salt lakes are agricultural alterations of vegetation and grazing patterns which can lead to changes in the salinity and composition of runoff and thereby affect the chemistry of lakes. Many examples of this have occurred in Western Australia (Williams, 1993).

The other major impact is the addition of pollutants to saline lakes. Almost the whole range of pollutants discharged to fresh waters is also discharged to salt lakes or their influent rivers. It is likely that the effect of these pollutants on salt lakes is essentially the same as on fresh waters. The modifying effects of salinity have, however, yet to be fully determined (Williams, 1993). Pollutants include nutrients from point sources and from non-point agricultural runoff, pesticides, and heavy metals resulting from mining and industrial activities. A number of examples of pollutants detected in saline lakes are given by Williams (1993). Other examples are given by Aladin (1993) and Reuter (1993).

2.6 Conclusions

This review has identified the major processes that control the water chemistry in saline lakes. Saline lakes may be defined as having a salinity of >3 g/L. Athalassic or inland saline lakes are those that have no direct connection, particularly in terms of biota, with marine waters. Saline lakes form as a result of the accumulation of salts derived mainly from soils and rocks of the catchment and from atmospheric transport of sea salts. Accumulation occurs in closed basins where evaporation balances inflow.

In closed basins, hydrological processes, sedimentation, water chemistry and mineralogy are intimately intertwined. The chemical composition of saline lake waters evolves with increasing evaporative concentration and is influenced by a number of processes which reflect

the interaction between these different components. The chemical fractionation that takes place between dilute inflow and the concentrated brines is accounted for by mineral precipitation, selective dissolution of efflorescent crusts and sediment coatings, sorption on active surfaces, degassing and redox reactions. The resultant water chemistry differs greatly between lakes, with the most important controlling factor being the composition of influent waters.

A number of minerals are precipitated from the waters of saline lakes. The most frequently occurring precipitates are carbonate minerals, which are usually the first to precipitate during evaporative concentration. With increasing evaporative concentration a wide range of evaporite minerals can form. A number of interactions between solid phases in the sediments and the water are important in controlling the concentrations of dissolved species, particularly the levels of N and P in the water.

Different saline lakes ecosystems, which are threatened by human activities that influence the water chemistry of the lakes, have been identified world-wide. Of these activities, the diversion of inflow waters with a consequent increase in salinity, is considered the most important. Saline lakes are also subjected to the introduction of pollutants, generated by human activities.

Chapter 3 Aqueous geochemistry of De Hoop Vlei

3.1 Introduction

The De Hoop Vlei ecosystem is an important wetland from a conservation point of view, particularly as a habitat for a number of species of water birds. Previous studies have shown that the aqueous chemistry of the De Hoop Vlei system is characterised by a high degree of spatial and temporal variation and have suggested that a number of geochemical processes play a role in controlling the water chemistry. An understanding of these processes is essential if the vlei ecosystem is to be effectively managed and the ecosystem conserved, because of the fundamental importance of the water to the vlei biota.

The objective of this chapter is therefore to characterize the aqueous geochemistry of the system and identify the different processes that play a role. A large part of the chapter focuses on an interpretation of the results obtained from water samples analyzed as part of this study. The chapter includes a description of the sampling procedure and the analytical techniques used. Interpretations are made in terms of geochemical processes that are considered to control the water chemistry. An analysis of hydro-chemical monitoring data collected over the last thirty years is also included in this chapter. These data allow for the identification of trends which occur over time. Geochemical modelling was used to model chemical equilibrium in the system. This gave an indication of processes likely to occur in the water as well as the behaviour of certain possible pollutants in the vlei.

3.2 Sampling

Water samples were taken during two separate sampling trips in 1996. The first took place from October 21 to 23, and the second from December 10 to 12. Water was sampled at a total of 27 locations. The position of each was determined using a Global Positioning System. A map showing the location of all sampling sites is given in Figure 3.1. Samples were collected in plastic bottles which were pre-rinsed at the sampling site. At least two samples were collected at each site, one of which was acidified using 50 percent nitric acid to facilitate subsequent cation analysis. At a number of sites duplicate samples were taken (ie a total of four). They were transported and stored at room temperature before analysis.

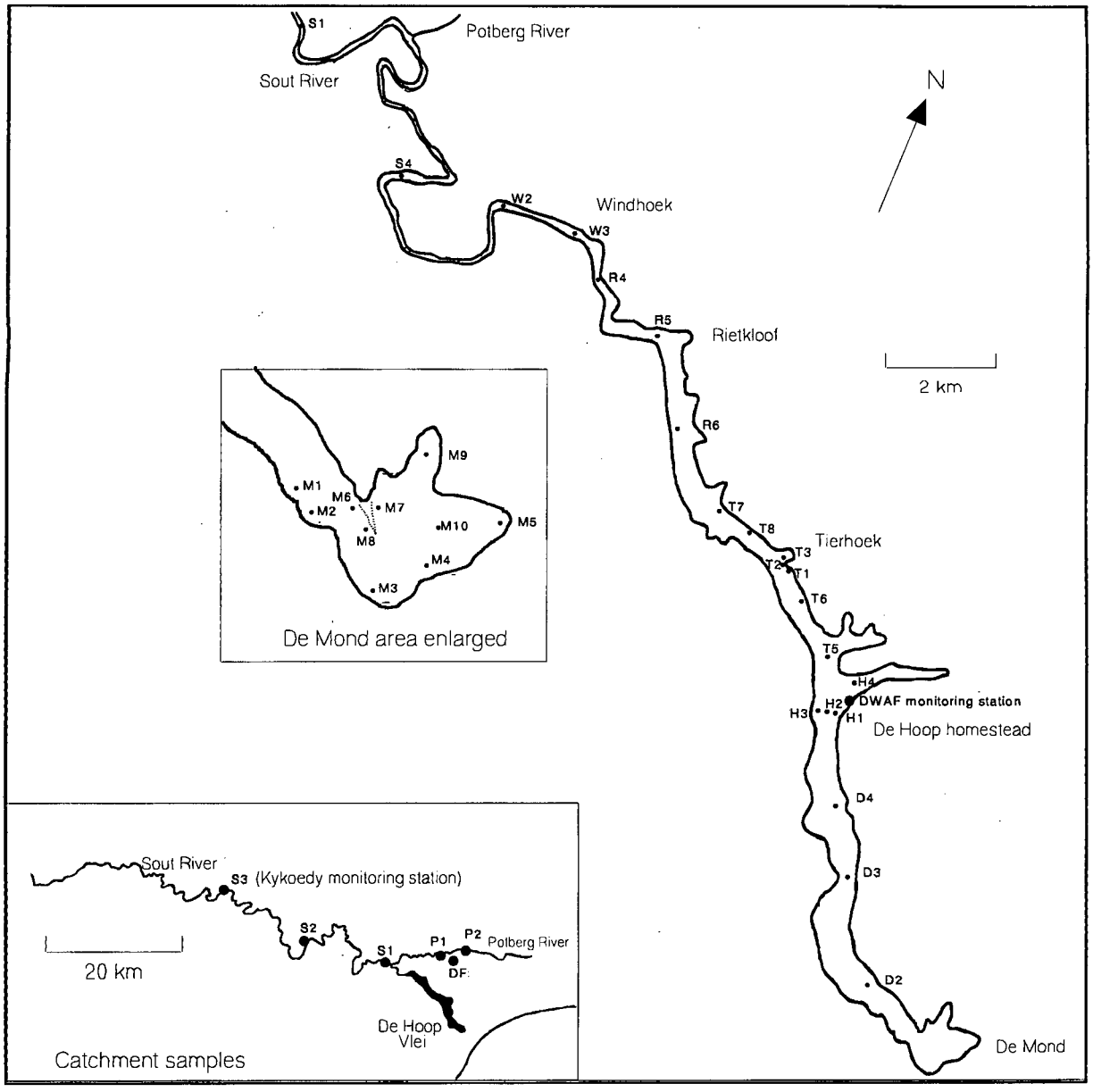

Figure 3.1 Map showing the location of all sampling stations within the study area.

Interstitial waters were obtained from sediment cores. After cutting and thawing frozen cores, interstitial water was extracted from the saturated sediment material under vacuum. Due to the low suction of the pump and the high matric potential of many of the sediments, sufficient interstitial water was obtained for only a few cores.

3.2.1 Sample numbers

To assist interpretation of results the following conventions were used in numbering samples (see Fig. 3.1). Each sampling site was assigned a letter describing its general position within

the study area followed by a number for the particular site. The following letters, arranged from south to north along the length of the vlei, were used:

M - De Mond area;
D - between De Mond and the vicinity of the De Hoop homestead;
H - the vicinity of the De Hoop homestead and campsite;
T - the area associated with the isolated Tierhoek spring water body;
R - in the vicinity of Rietkloof between the Tierhoek water and the water in the north of the vlei at Windhoek;
W - the water body in the vicinity of the Windhoek farmhouse;
S - the Sout River
P - the Potberg River
DF - a single groundwater sample from Driefontein farm

Interstitial waters are denoted by an I in front of the sample number and are further characterised by the lower depth of the core section in millimetres given after the sample number. All samples collected during the second sampling trip are indicated by a 2 after the sample number.

3.3 Analytical methods

The analytical procedures carried out on each sample are described individually below. All the methods except the use of high performance ion chromatography (HPIC) and inductively coupled plasma atomic emission spectrometry (ICP-AES) follow the standard methods given in Standard Methods (1985) from which details of the methods may be obtained. All samples were filtered through a 0.22 μm filter prior to analysis to remove suspended particulate matter. Electrical conductivity and pH were, however, measured before filtration. All analyses except ICP-AES were performed on non-acidified samples. Samples from the first sampling trip were analyzed before the second sampling trip. Interstitial waters were analyzed with the second set of samples. All samples were transported to the laboratory at room temperature after which they were stored under refrigeration at 4°C.

To ensure the accuracy and precision of all analyses the following procedures were followed. Certain water samples were collected and analyzed in duplicate. During analytical runs certain samples were analyzed in duplicate and standards were run to assess accuracy. During the analysis of the second set of samples, samples from the first collection were repeated to check for consistency between runs. Finally a charge balance was calculated for each water sample

to check for accuracy. Details of the results of these procedures and indications of the precision and accuracy of data are given in Appendix 1. Data were only used when these procedures indicated acceptable levels of error. All charge balances were within ten percent.

3.3.1 Electrical conductivity (EC)

Electrical conductivity was measured electrometrically using a Crison microCM 2201 EC meter with conductivity electrode and temperature sensor for temperature correction. EC values are reported at a reference temperature of 20°C. Electrical conductivity standards (12.88 mS/cm and 1433 μS/cm at 25°C) were measured prior to sample analysis.

3.3.2 pH

pH was measured using a Crison micropH 2001 pH meter with combined glass-calomel electrode. The pH meter was calibrated against standard buffer solutions before use.

3.3.3 Alkalinity

Alkalinity is a measure of the capacity of the water to neutralise an addition of acid. For the water under discussion this is approximately equal to the total dissolved carbonate concentration. It was measured by end-point titration to pH 4.5 using standard 0.01M HCl and a Radiometer TTT85 auto titrator. The procedure involved determining the volume of HCl required to titrate 10 mL of each sample to the end point pH.

3.3.4 Dissolved phosphorus concentration

Phosphorus concentration was measured using the ascorbic acid method and the exact procedure given in Standard Methods (1985) was followed. This involves the formation of a blue coloured phospho-molybdate complex by reaction with a combined potassium antimonyl tartrate, ammonium molybdate and ascorbic acid reagent, and its subsequent concentration determination by colorimetry. For this, absorbance was measured at 880 nm using a TURNER Model 340 spectrophotometer, and P concentration was calculated for the samples from a calibration curve set up using the absorbance of solutions of known P concentration. All glassware was acid washed prior to analysis in order to minimize P contamination. Standards were analyzed with every analytical run.

3.3.5 Fluoride concentration

Fluoride concentration was measured using a Corning ion analyzer 255 with fluoride selective electrode containing a LaF_3 crystal and a calomel reference electrode. Each 10 mL water sample was mixed with 10 mL of a total ionic strength adjustment buffer (TISAB) prior to analysis. A three-point calibration was performed using standard F solutions of 10, 1.0 and 0.1 ppm F^-.

3.3.6 Major cation and anion concentrations using HPIC

High performance ion chromatography (HPIC) involves the separation of the ions in eluent on an exchange separator column and the comparison of the peak heights to calibration curves set up with solutions of known ion concentrations. Separate runs are done for cations and anions. Ions measured were the cations Na^+, Ca^{2+}, Mg^{2+}, K^+, and NH_4^+ and the anions Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, and Br^-.

All samples were diluted with deionised water to obtain EC values < 10 mS/m. Immediately prior to analysis, the samples were passed through a Dionex On-Guard-P cartridge for the removal of organic colloids. A DIONEX 3000 ion chromatograph and DIONEX API-450 software were used. Cation separation was achieved using a DIONEX HPIC-CS5 exchange column with 20mM methyl-sulphonic acid eluent. Flow rate was 1.0 $mL.min^{-1}$. Anions were determined using a Dionex HPIC-IonPac AS4A-SC ion exchange column using 1.80 mM Na_2CO_3 and 1.70 mM $NaHCO_3$ eluent. Flow rate was 2.0 $mL.min^{-1}$. MicroMembrane™ cation and anion autosuppressors were used.

Four standards were analyzed at the start of each analytical session and deionised water was included as a blank.

3.3.7 Major cations and trace metals using ICP-AES

The total elemental concentrations of major cations for certain samples, and trace metals were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES). Analyses were performed in two separate runs for first and second water samples using different instruments. Elements analyzed in the first samples were Na, Mg, Ca, K, Si, Al, Ni, Pb, Fe, Mn, Zn, Cu, Cd, Co and Cr. These analyses were done in the Chemistry Department of the University of Cape Town using a Jobyn Yvon 70C(JY70C) combined simultaneous/sequential ICP spectrometer coupled with J-Yess version 4.0 software. The

following instrumental settings were used: Power, 1Kw; Pressure - Ar gas, 3.4 bar; R.F., 27.12 MHz; Flow rate, 2.0 ml/min; Aerosol gas flow, 0.4/min and 0.8/min (Na and K); Plasma gas flow, 0.1 ml/min; Coolant gas flow, 16 ml/min.

Elements analyzed in the second samples were Si, Al, Ni, Pb, Fe, Mn, Zn and Cu. These analyses were done in the Archaeology Department of the University of Cape Town using a Jobyn Yvon JY-138 ULTRACE spectrometer.

3.3.8 DWAF data base

Use was made of an historical record of analyses performed by the Department of Water Affairs and Forestry (DWAF) on samples collected from two monitoring stations, one on De Hoop Vlei and the other at Kykoedy on the Sout River. The De Hoop Vlei samples were collected from July 1965 to November 1995 and comprised a total of 159 samples. Those at Kykoedy were collected from July 1965 to November 1996 and numbered 246 in total. These data are given in Appendix 3. In these samples metals were analyzed by atomic absorption spectrophotometry, chloride and alkalinity titrimetrically and TDS and sulphate gravimetrically. Details of the analytical methods can be found in van Vliet *et al.* (1988).

3.4 Results and discussion

Results of pH, EC and major ion analyses performed on the water samples are given in Table 3.1. Several water samples were analyzed only for pH and EC. The results of these are given in Table 3.2. By examining the results in terms of the locations at which each was sampled (Fig. 3.1), it is evident that there are large differences in water chemistry at different locations within the sampling area. These differences include differences in pH, salinity and relative proportions of major ions. Variation along the length of the vlei is evident so that three distinct type of waters are distinguishable within the vlei. The waters of the catchment are also distinguished from those of the vlei for discussion purposes. Water samples included interstitial sediment waters which are also dealt with as a separate group in the discussion. Results of the pH, EC and major ion analyses performed on the interstitial waters is given with those for the corresponding overlying bulk waters for comparison, in Table 3.3. In general the waters of De Hoop Vlei and its catchment are alkaline and are either saline with Na and Cl as dominant ions or non saline with higher proportions of Ca and carbonates.

Table 3.1. pH, EC and major ion concentrations in water samples from De Hoop Vlei and its catchment. TDS was calculated by the summation of major ions. All concentrations are given in mg/L. The locations of all sampling sites are shown in Figure 3.1.

Sample	pH	EC (mS/m)	TDS	Na	Mg	Ca	K	Cl	SO_4	Alkalinity as HCO_3
Vlei										
M3	9.6	1837	12252	4130	447	29	60	6567	579	441
M5	10.0	1698	11749	3805	391	24	55	6445	581	449
M5-2	9.7	2500	18415	5905	821	341	103	9858	864	523
M6	9.8	2080	14357	4708	491	32	64	7895	673	496
D3-2	9.8	1763	12584	3745	700	179	73	6682	722	482
D4-2	9.5	1373	9657	2719	594	182	77	4841	964	281
H1	9.0	692	4887	1344	232	95	36	2291	546	343
H1-2	8.3	3070	24211	7172	1555	475	153	12296	2109	451
H4	9.2	480	3182	892	164	104	20	1351	452	199
T1	8.0	86	551	84	10	71	3	172	19	190
T2	8.3	87	554	84	10	68	3	177	26	186
T3	7.7	149	1051	175	26	116	5	309	14	406
T7-2	9.0	846	6404	1830	415	148	44	2863	948	158
W3-2	8.2	2630	20036	6100	1265	459	136	10341	1060	675
W2-2	8.2	2490	18872	5724	1119	312	122	9945	956	694
Catchment										
P1	8.3	1685	11443	3463	435	195	59	6103	659	529
P2	8.1	708	4542	1350	153	105	33	2353	255	293
P4	8.3	1505	9524	2880	361	159	54	5051	560	459
S4-2	8.2	2160	16329	5064	950	264	86	8510	676	779
S1	8.8	1373	8621	2620	311	68	51	4724	353	494
S1-2	8.2	1707	12848	3952	763	246	74	6536	471	807
S2	7.5	1333	8763	2845	355	109	34	4461	395	564
S3	8.1	1396	8984	2810	321	62	45	4747	366	633
DF	8.0	163	1066	174	19	149	4	386	58	275

The letter in the sample name describes its general position within the study area while the number indicates the particular site (see Fig. 3.1). All samples collected during the second sampling trip are indicated by a 2 after the sample number.

Table 3.2 Results of the analyses of water samples from De Hoop Vlei and catchment which were analyzed only for pH and EC.

Sample	pH	EC (mS/m)
M6-2	9.3	2350
D2-2	9.4	2290
T5-2	8.2	89
T6-2	8.4	90
T1-2	7.9	85
T2-2	8.3	85
T8-2	9.6	629
P3	7.8	65

3.4.1 Salinity

Electrical conductivity (EC) was measured in the laboratory as an indication of salinity. Salinity was also estimated by the summation of individual ion analyses. Only the eight major ions with carbonates recalculated as HCO_3 from alkalinity values were used for this calculation. The results for the waters of the vlei show a range of EC values between 86 and 3070 mS/m with corresponding salinity values between 0.55 and 24.21 g/L. Results for the catchment range between 65 and 2160 mS/m with corresponding values between 0.35 and 16.33 g/L. Interstitial waters had higher salinity than the overlying bulk waters in all cases.

3.4.1.1 Spatial variation

By examining variation along the length of the vlei it is evident that EC values from the southern part of the vlei at De Mond are consistently high in the region of 2000 mS/m. In comparison with the historical record from DWAF data, such values are high, but are to be expected due to the low water level which occurred at the time of sampling. EC decreases in a northerly direction away from the De Mond area, reaching a minimum at the Tierhoek spring (sample T1). The one exception to this is the very high EC of the second water sample taken at H1 (3070) mS/m). This value can, however, be explained by the fact that this sample

Table 3.3 Comparison of the pH, EC and major ion concentrations in interstitial and overlying bulk waters from De Hoop Vlei. All concentrations are in mg/L. Blank values indicate that analyses were not done.

Sample	pH	EC (mS/m)	TDS	Na	Mg	Ca	K	NH_4	Cl	SO_4	HCO_3
M3	9.6	1837	12252	4130	447	29	60	0	6567	579	441
IM3-100	8.2	2210	16449	4635	947	191	116	86	8170	509	1795
IM3-260	8.5	2210									
M5	10.0	1698	11749	3805	391	24	55	0	6445	581	449
IM5-150	8.0	1884	13997	4044	891	205	94	61	6811	957	934
IM5-280	8.0	2220									
M9	9.9	1917									
IM9-120	8.2	2180									
T2	8.3	87	554	84	10	68	3	0	177	26	186
IT2-210	7.2	270	2466	273	147	313	24	31	240	1036	401

Interstitial waters are denoted by an I in front of the sample number and are further characterised by the lower depth of the core section in millimetres given after the sample number.

was taken at the extremity of northerly surface water cover at the time and in very shallow water (10 cm) compared to much greater water depths further south (in the order of 1.5 m). There was, therefore, potential for a higher degree of evaporative concentration at this point than at the sample stations further south, which would explain the higher EC value obtained.

Spatial variation in salinity in the Tierhoek area is limited. South of Tierhoek, when this water body was isolated from other surface waters in the vlei, EC varied only between 85 at the source of the spring and 89 mS/m further south. The variation in the Tierhoek water body north of the spring is much greater and increases northwards to a value of 846 mS/m (sample T7). The relative constancy of the salinity at Tierhoek suggests that the water further north receives salinity from another source or is concentrated through evaporation. It is possible that evaporation could affect the water north of Tierhoek differently to that south of the spring. During the second sampling trip (when this water body was isolated) there was a southerly flow direction south of the spring while the water to the north seemed stationary. It would therefore be subject to a longer period of evaporation, giving rise to higher EC values. Alternatively it could be fed from a different groundwater source with a higher salinity.

The electrical conductivity of water at the northern end of the vlei in the Windhoek region is similar to that at the southern end. The maximum measured value in the Windhoek area was 2630 mS/m and occurred at the southern extremity of surface water coverage in the area. Values decreased northwards up the vlei and in the lower parts of the Sout River. The increasing salinity southwards could be explained by the increasing effect of evaporative concentration as water enters, spreads out and stops flowing within the vlei.

The salinity of the catchment waters is high. Values for the Sout River vary between 1333 and 2160 mS/m while those of the Potberg River show greater variation. The sample with the lowest salinity of 65 mS/m, P3 was taken from fresh runoff water from agricultural lands during a period of high rainfall following several days of rain and would therefore be expected to be low. Because of the rainy conditions at the time of sampling other values represent a range of salinities from fresh runoff to water subjected to evaporative concentration. The first runoff from lands where salts had accumulated over a long dry period would be expected to be high and may also contribute to the salinities of some of the samples. The higher values for Potberg samples are higher than those of the Sout River. Sample DF is a groundwater sample from a limestone environment in the Potberg River valley and is significantly lower than surface waters of the area. This difference can be accounted for by differences in the soluble salt content of the limestones and the shales.

The high salinity of the catchment waters is probably the result of a combination of the geology of the catchment and its proximity to the coast. Salinity in the rivers may also be affected by evaporative concentration. The weathering of shales with a high soluble salt content and inputs of salts from wet and dry atmospheric deposition would both cause high salinities. Agricultural practices could also be responsible for increasing the salinity of runoff waters through fertilizer applications and alterations in the hydrological and weathering systems.

The EC of all four interstitial waters sampled is higher than that of the overlying bulk water. Such a condition has been reported by Knesl (1996) for the interstitial waters of Barbers Pan. Concentration factors vary between 1.1 and 1.3 for the De Mond samples with the more dilute Tierhoek sample having a higher concentration factor of 3.1. Results of the variation of EC with depth in interstitial water are inconclusive with IM3 showing no increase with depth while IM5 increases from 1884 to 2220 mS/m with a 13 cm increase in depth. The higher salinity in the interstitial water provides potential for diffusion of salts into the bulk waters from the sediments, particularly during times of lower salinity inflow into the vlei. Such a process is described by Lerman and Jones (1973). It would provide an additional mechanism to evaporative concentration for increasing the salinity of the waters in the vlei following inputs of lower salinity water. It also means that mineral saturation would vary between the bulk and interstitial waters so that precipitation could occur in the sediments, while not occurring in the bulk water.

Spatial variation of salinity in the vlei is adequately explained by the mixing of high and low salinity inflow waters and by evaporative concentration. From the data presented, the following model is proposed. Water of high salinity enters the vlei from the Potberg and Sout Rivers in the north. This water mixes with water of lower salinity from groundwater springs such as the one at Tierhoek, resulting in water of intermediate salinity. Samples taken in the De Hoop area during the first sampling period, when greater surface coverage resulted in mixing with the Tierhoek waters, showed salinities intermediate between the river and groundwater inputs suggesting such a mixing process. After inflows cease evaporative concentration results in the increase of salinity in the surface water which remains. This model is validated by an examination of the major ion chemistry which also distinguishes the different types of waters discussed here.

3.4.1.2 Temporal variation

Temporal variation in salinity is indicated by differences between two samples from the same

location collected during the first and second sampling trips. All stations sampled south of the Tierhoek water body showed an increase in EC between the first and second sampling. This can be explained by evaporative concentration. The fact that samples taken at S2 also showed an increase indicates that evaporative concentration plays a part in the salinity of the rivers as well as the vlei. Increases indicate a concentration factor of between 1.1 for M6 and 4.4 for H1. Samples from the Tierhoek area showed no change in salinity between the two sampling periods indicating that the spring water quality was unaffected by rainfall or evaporative concentration. The temporal variation in salinity in the vlei and at Kykoedy on the Sout River is also evident from the DWAF data record. Recorded variation in the vlei is between 344 and 2222 mS/m and at Kykoedy is between 101 and 1803 mS/m. Monitoring of the salinity and water depth have shown an inverse relationship between the two parameters (Scott and Hamman, 1988) and therefore suggests that increasing salinity is the result of evaporative concentration.

Because of continual salt inputs to the vlei, an increase in salinity over the long term would be expected if no mechanisms for salt removal operated in the system. Proposed mechanisms of removal in saline lakes include deflation and the covering of chemical sediments by clastic sediments introduced during storms or the deposition of aeolian sediments (Hammer, 1986). A linear fit of salinity over time was performed by PD Toens and Associates (1994b) and showed a slight increase in salinity. The regression was not, however, statistically significant. An attempt to identify any trend by plotting EC against water depth and investigating the relationship between these parameters over different periods was inconclusive because of the lack of a close correlation between the parameters. The plot is given in Figure 3.2.

An evaluation of salinity trends using water depth must take into account the fact that lake level does not equate with lake volume due to sedimentation and reduced basin capacity. This process would, however, serve to increase any trend of increasing salinity. These results suggest that salt inputs are in balance with salt outputs in the De Hoop Vlei system. The historical record may, however, not be of sufficient duration to quantitatively demonstrate such a trend. An alternative mechanism of salt removal that may operate at De Hoop is the movement of high salinity water as groundwater flow to the sea.

3.4.1.3 Classification of the water in terms of salinity

Because of the large variations in salinity discussed above, it is difficult to distinctly classify De Hoop Vlei in terms of salinity. According to the classification of saline lakes discussed in section 2.2, the vlei south and north of Tierhoek would generally be classified as

hyposaline having a salinity between 3 and 20 g/L. The water body at Tierhoek with salinity around 0.5 g/L would be borderline between fresh and subsaline. Examination of the DWAF data shows that salinity occasionally drops below 3 g/L. Such an occurrence is only likely to occur immediately after heavy rains. The water body remaining in the south of the vlei during dry spells would be mesosaline with a salinity > 20 g/L. Of the samples collected during this study, several at De Mond and one in the north of the vlei had salinities > 20 g/L.

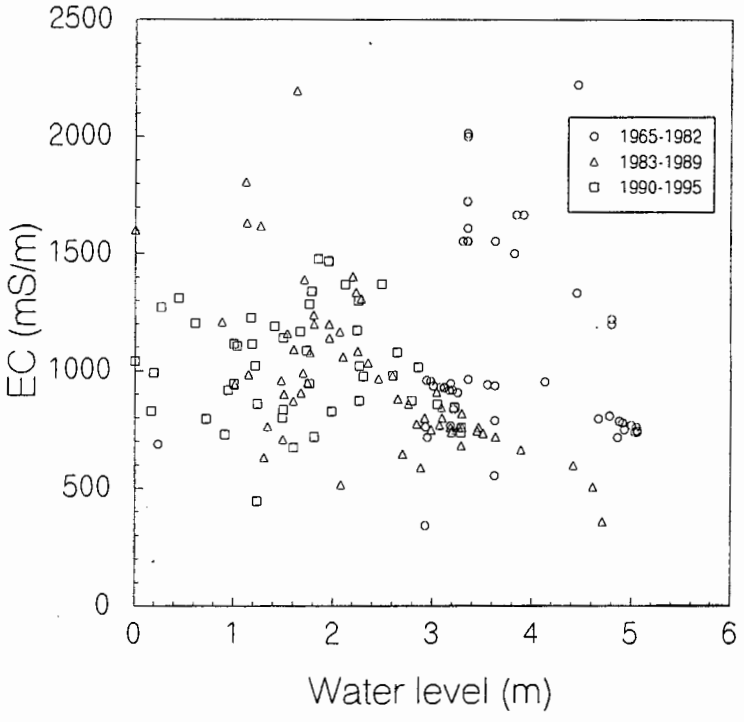

Figure 3.2 Plot showing the relationship between water depth in the vlei and EC for different periods in the historical record.

3.4.2 pH

All waters of the vlei and catchment are alkaline with pH values varying between 7.7 and 10.0 for the vlei water and between 7.5 and 8.8 for the waters of the catchment. De Hoop has high pH compared to other Southern African saline water bodies discussed by Seaman (1991). In the vlei, the highest pH values occur in the De Mond area. As discussed above this is where the evolution of brine occurs to the greatest extent. Brine evolution in De Hoop Vlei follows path I of the Hardie-Eugster model (see section 3.4.8) and therefore, as discussed in section 2.4.2, the production of an alkaline brine is expected. Another factor affecting pH is the biological utilisation of CO_2 (which also increases pH). The rate of photosynthesis will

therefore affect pH and both daily and seasonal variation is to be expected. Diurnal variation in pH has been recorded in De Hoop Vlei by Coetzee (1986).

The effect of carbonate precipitation on pH is possibly evident in comparing the Tierhoek waters with those from De Mond. At Tierhoek, where the Ca ion activity is high, the pH is in the region of 8. Following $CaCO_3$ precipitation and Ca depletion at De Mond, the pH increases to > 9.5. This effect can also be seen by comparing the difference between first and second water samples in the southern part of the vlei. As has been discussed above, the first water samples represent a more advanced state of brine evolution following a long period of evaporation while the second samples represent water characteristic of more recent inputs of water into the vlei, with higher Ca concentrations. In the three cases where repeat samples were taken on the second sampling trip, pH had dropped by between 0.3 and 0.7 pH units. The higher pH at the time of first sampling can be explained by the evolution of the water following a long period of evaporative concentration.

The same effect is evident on examination of the DWAF data. Figure 3.3 shows the relationship between Na/(Na + Ca), a ratio used by Day (1993), and pH. The ratio Na/(Na + Ca) is a measure of the extent to which Ca has been depleted relative to other cations in the water following $CaCO_3$ precipitation. Although the correlation is not significant (R^2 = 0.233) there is evidence of a trend of increasing pH as Ca is depleted in the water. The poor correlation could be the result of other factors influencing the pH.

The lowest pH in the vlei water is in sample T3 (see Table 3.1). This could be a result of dissolved fulvic acid in the water as it showed distinct brown coloration compared to other samples. Higher fulvic acid concentration in this sample could be a result of a large mass of organic material and a more prolonged and intimate contact between this and the water in this sampling position. The samples were taken where shallow, stagnant water had inundated an area of high reed growth. Other samples in the area were taken in channels of more open water.

The pH of all interstitial waters is between 1.1 and 2 pH units lower than that of the overlying bulk water (see Table 3.3). Lower interstitial pH values have been measured in other studies (Knesl, 1995). This can possibly be explained by anaerobic conditions in the sediments and a slow rate of gas exchange between sediments and water. This would lead to an increase in the production of CO_2 and of protonated species following anaerobic oxidation of organic matter and therefore cause a lowering of pH (Ben-Yaakov, 1973; Mackenzie *et al.*, 1995). From the two cases where it was determined, there is no indication of a change in pH

with depth in the sediment.

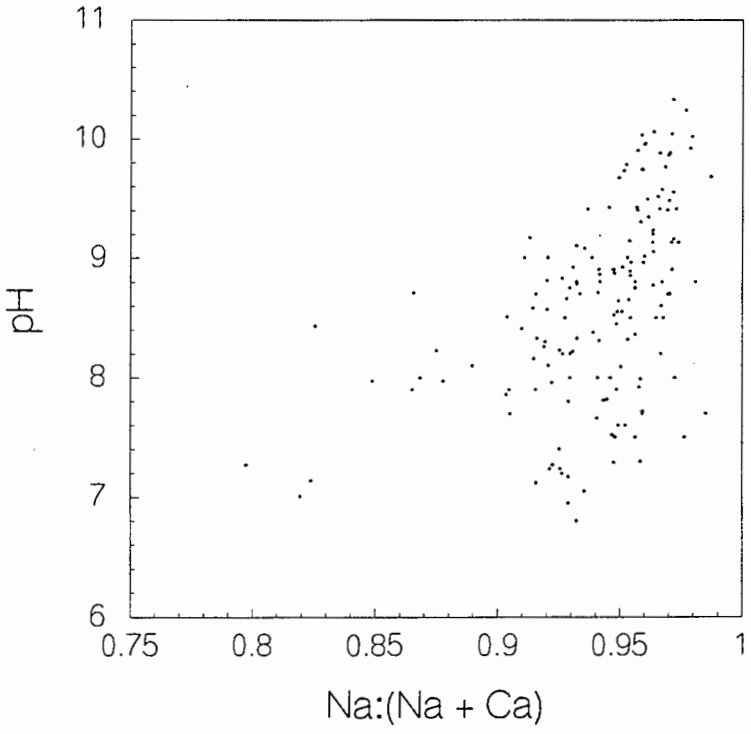

Figure 3.3 Plot of pH against Na:(Na + Ca) for the DWAF data from De Hoop Vlei.

3.4.3 Major ion chemistry

Table 3.4 gives the relative proportions of the major ions in all the water samples. Differences in ion proportions can be explained by the varying effects of geology and evaporative concentration on the different samples. Although the proportions of the major ions vary considerably through the study area Na is the dominant cation and Cl the dominant anion in all the samples except one interstitial water. According to Day (1993) these are the dominant ions in all fresh and saline waters on the south and east coasts of South Africa.

3.4.3.1 Cations

Sodium dominance in the vlei waters south of Tierhoek varies between 66 and 83 percent with the highest Na dominance occurring in samples from the De Mond area taken during the first sampling period. These samples with the highest Na dominance have the cation concentration sequence Na > Mg > K > Ca. Other samples in this area but from further north or taken during the second sampling period have lower Na dominance (maximum 74 percent) and the concentration sequence Na > Mg > Ca > K. This is the same sequence as indicated by the DWAF data for the vlei. Of the cations, Ca proportions show the greatest relative

differences. Differences in the Ca proportion between first and second samples are particularly evident in the De Mond area compared to other parts of the vlei (see Table 3.4).

Table 3.4 The proportions of the major ions in water samples from De Hoop Vlei. All values are in percentage equivalents of the cation or anion total. The Mg:Ca is the equivalent ratio.

Sample	Na	Mg	Ca	K	Cl	SO_4	HCO_3	Mg:Ca
Vlei								
M3	81.9	16.8	0.7	0.7	90.6	5.9	3.5	25.1
M5	82.6	16.0	0.6	0.7	90.3	6.0	3.7	26.7
M5-2	74.6	19.6	4.9	0.8	91.3	5.9	2.8	4.0
M6	82.4	16.3	0.6	0.7	91.0	5.7	3.3	25.7
D3-2	70.4	24.9	3.9	0.8	89.2	7.1	3.7	6.4
D4-2	66.4	27.4	5.1	1.1	84.7	12.4	2.9	5.4
H1	70.2	22.9	5.7	1.1	79.2	13.9	6.9	4.0
H1-2	66.7	27.4	5.1	0.8	87.1	11.0	1.9	5.4
H4	66.9	23.3	9.0	0.9	75.0	18.6	6.4	2.6
T1	44.9	10.2	43.8	1.1	58.0	4.8	37.2	0.2
T2	45.6	10.7	42.6	1.1	58.2	6.3	35.6	0.3
T3	48.6	13.6	36.9	0.9	55.7	1.8	42.5	0.4
W7-2	65.1	27.9	6.0	0.9	78.3	19.1	2.5	4.6
W3-2	67.0	26.3	5.8	0.9	89.8	6.8	3.4	4.5
W2-2	69.2	25.6	4.3	0.9	90.0	6.4	3.6	5.9
Catchment								
P1	76.2	18.1	4.9	0.8	88.5	7.1	4.5	3.7
P2	75.9	16.3	6.8	1.1	86.8	6.9	6.3	2.4
P4	76.3	18.1	4.8	0.8	88.1	7.2	4.7	3.8
S4-2	70.2	24.9	4.2	0.7	89.9	5.3	4.8	5.9
S1	79.0	17.7	2.4	0.9	89.6	4.9	5.4	7.5
S1-2	69.1	25.2	4.9	0.8	88.9	4.7	6.4	5.1
S2	77.7	18.3	3.4	0.5	87.8	5.7	6.4	5.4
S3	80.0	17.3	2.0	0.8	88.2	5.0	6.8	8.6
DF	45.3	9.6	44.5	0.6	65.5	7.3	27.2	0.2
Interstitial								
IM3-100	67.9	26.3	3.2	1.0	85.2	3.9	10.9	8.2
IM5-150	66.3	27.6	3.9	0.9	84.5	8.8	6.7	7.2
IT2-210	28.3	28.9	37.3	1.5	19.4	61.8	18.8	0.8

The following explanation is proposed for these differences. At the time of the first sampling, the De Mond area had been subjected to evaporative concentration for a long period which resulted in $CaCO_3$ precipitation and Ca depletion in the water column. In section 3.4.8 it is

shown that, according to the chemical divide theory of Hardie and Eugster, Ca should be depleted relative to other major ions by $CaCO_3$ precipitation. Rain which fell during the first sampling resulted in the mixing of vlei water with water from the Tierhoek spring which has a high Ca concentration, and higher Ca concentrations were therefore introduced into the vlei. In-flow from the rivers also contains greater proportions of Ca compared to the evaporated vlei water. These higher Ca concentrations were detected in samples taken in the De Hoop area (H samples) during the first sampling period. However, the Tierhoek water had not yet mixed with water further south in the De Mond area when the first samples were taken. By the time the second samples were taken, the fresh inputs and mixing of higher Ca water following the rainy period had resulted in higher Ca proportions throughout the vlei.

Such an explanation assumes a kinetic limitation on Ca precipitation, such that very little precipitation would have occurred in the period between sampling trips. This may be a result of a slow precipitation process or precipitation only occurring at certain times during the year. Rosen *et al.* (1995), found that Ca precipitation in a saline lake only occurred at certain times of year and only during periods of high biological activity.

Results from the samples taken at H1 support the hypothesis that very little Ca precipitation took place between the two sampling trips. Although evaporation of the water here caused a five-fold concentration (according to calculated salinity values) and resulted in supersaturation of the water with respect to $CaCO_3$ minerals, there was very little change in the Ca proportion from 5.7 to 5.1 percent. This suggests either that the period was too short or that conditions at the time were unsuitable for significant Ca precipitation.

The samples from Tierhoek show major departures from the other vlei waters with respect to their cation proportions. The cation concentration sequence here was Na > Ca > Mg > K and the proportion of Ca was only marginally smaller than that of Na. Sample T1 was taken from the outflow of the spring and therefore represents water of a composition which is strongly influenced by the host rock composition. The high Ca is to be expected in water from a limestone environment. The high Na is, however, evidence of the effect of sea salts on the composition of rainfall and therefore groundwater recharge. Sample T1 is similar to DF which is also a ground water sample from a limestone environment. The other samples from the vicinity of the spring are very similar to T1, suggesting that they are not influenced greatly by evaporative concentration and mineral precipitation. The composition of T5 is, however, very different, with the cation composition being similar to that of waters from the northern end of the vlei, having much lower Ca proportions and the cation sequence Na > Mg > Ca > K. The difference between this sample and the other Tierhoek samples has already

been discussed under the section on salinity. The lower Ca proportions could be explained by Ca precipitation since the spring water is supersaturated with respect to aragonite, calcite and dolomite (see section 3.3.7). Another possible explanation for these differences lies in the interaction of spring water with clastic sediments deposited during high water levels and, therefore, not in equilibrium with the spring water but rather with water of a higher salinity and with a different ionic composition.

The waters from the Windhoek area and from the catchment are similar in cation composition to those other vlei samples in which Ca has not yet been depleted by evaporative concentration and Ca transfer to the sediments. The cation composition of these waters is also similar to that of sea water.

The cation composition of the interstitial waters differs from that of the overlying bulk water. Ammonium, which was below detection limits for all bulk waters, was detected in all of the interstitial water samples. Nitrogen is discussed further in section 3.4.5.1. Interstitial waters from the De Mond area have higher Ca and Mg proportions and lower Na proportions than bulk water samples from the same area. The higher Ca proportions could be caused by the effect of lower pH and increased CO_2 concentration on $CaCO_3$ solubility. Changes in pH and CO_2 in interstitial waters are likely to be brought about by anaerobic breakdown of organic matter. Interstitial waters are also not directly affected by evaporative concentration. The interstitial waters sampled in the De Mond area are characteristic of vlei waters not affected by evaporative concentration. The interstitial water from the Tierhoek area has lower Ca and Na proportions than the bulk water but a higher Mg proportion.

In terms of major ion speciation, the water chemistry of De Hoop Vlei is complex with high proportions of certain elements occurring in species other than their free ions. The speciation of major ions, unlike that of potentially toxic trace elements, is not, however, important to the consideration of water chemistry in this study. The programme MINTEQA2 was used to model the speciation of elements occurring in the water. To give an indication of the complexity of speciation, the results of this speciation for the major ions are given in Appendix 5. The speciation of trace elements is considered in section 3.4.6.

3.4.3.2 Anions

Chloride is the dominant anion in all surface waters with dominance in the order of 90 percent for the water at De Mond and marginally lower for all other waters excluding those influenced by the Tierhoek spring. Tierhoek waters have a far lower chloride dominance in

the order of 58 percent with carbonate species making up between 36 and 43 percent. This is due to the influence of the limestone environment discussed above. The majority of vlei waters have the anion sequence $Cl > SO_4 > (HCO_3 + CO_3)$ as do the waters of the Potberg River. The Tierhoek waters and those of the Sout River have the sequence $Cl > (HCO_3 + CO_3) > SO_4$, although the Sout River samples have much lower carbonate proportions than those of Tierhoek. The difference in relative amounts of sulphate and carbonate between the Potberg and Sout rivers could be the result of the Potberg catchment receiving greater amounts of sulphate from atmospheric deposition due to its greater proximity to the ocean.

In the interstitial waters at De Mond the carbonate proportions are higher than those of the bulk waters, as are the proportions of Ca already discussed above. Higher carbonate may result from the production of CO_2 by anaerobic oxidation of organic matter in the sediments. Like Ca, it may also be the result of an increase in $CaCO_3$ solubility at lower pH. Sample IT2 has a particularly high proportion of sulphate.

Because evolution of the De Hoop water appears to have followed path I of the Hardie-Eugster model (see section 3.4.8), the relative proportion of carbonate is not depleted to the same extent as that of Ca by $CaCO_3$ precipitation. The carbonate concentration is also influenced by a number of additional processes including degassing of CO_2 and biological oxidation of organic matter. The influence of $CaCO_3$ precipitation on the variation in carbonate proportions (Table 3.4) is, therefore, not as evident as it is on the variation in Ca proportions. Carbonate proportions however, show a decrease with increasing salinity and between the first and second sampling.

Loss of SO_4 from the waters of saline lakes, in the absence of precipitation of sulphates, occurs predominantly by reduction to sulphides in the sediments (Hammer, 1986). Sulphate proportions in the samples between De Mond and Tierhoek are generally higher than elsewhere with a maximum at H4. This sampling site is in an area which was covered by water during recent rains and which had dried out by the second sampling period. There would have been less opportunity for reduction of sulphate at this site because of the short period of inundation as well as the relatively shallow water depth. The other sites characterised by a high sulphate concentration were also shallower than the sites at De Mond which had lower SO_4 levels. Sample T7-2 had the highest sulphate proportion of all surface water samples.

The predicted anion speciation using MINTEQA2 is given in Appendix 5. All Cl occurs in the form of the free ion. The forms of sulphate predicted to occur are the SO_4^{2-} anion as well

as Ca, Mg and Na sulphates. Carbonate species occur predominantly in almost all water samples as the bicarbonate ion except in sample M5-2, where $MgCO_3^0$ is the dominant form. Other species of carbonate include Ca, Mg and Na carbonates and bicarbonates.

3.4.4 Origin of the salts in De Hoop Vlei

The high Na and Cl dominance in all water samples, including those not subjected to evaporative concentration, such as groundwaters, can be attributed to marine influence. This suggests that significant quantities of Na and Cl are transported into the catchment through wet or dry atmospheric deposition. This is recognised as an important source of salts in saline coastal lakes (Hammer, 1986). These salts are then transported by waters of the catchment to De Hoop Vlei. The high salinity of the catchment waters, even during periods of high rainfall such as occurred during the first sampling,is evidence of the significant contribution of sea salts. Furthermore, the fact that groundwater samples from limestone environments (samples T1 and DF) also have Na and Cl as dominant ions, suggests that groundwater recharge derives from NaCl dominated water.

The Bokkeveld shales of the catchment area can also be expected to contribute significant amounts of salts to the vlei. As evidence of this contribution, groundwaters in the shales have been found to have high salinities dominated by Na and Cl, making them unsuitable for domestic or agricultural use (PD Toens and Associates, 1994a). It is likely that calcium and bicarbonate ions originate predominantly from the dissolution of limestones and are transported to the vlei by groundwater movement and discharge into the vlei.

It is possible that some salts are relic from sea waters originally trapped in the vlei at the time it was cut off from the sea. Significant discharge of water from the vlei towards the sea via groundwater would, however, limit the presence of these over time.

3.4.5 Nutrients

3.4.5.1 Nitrogen

Although HPIC analysis was set up for the determination of both nitrate and nitrite, these were below detection limits in all samples. Samples had to be diluted up to 250 times for the analysis so it is to be expected that low nitrogen concentrations would have been diluted below detection limits. Examination of the DWAF data shows that values for N (as NO_3 + NO_2) are usually less than 0.5 and often below 0.1 mg/L, but with occasional values as high

as 5 mg/L and one of 12 mg/L which could be an error. Ammonium N values are generally higher than N as nitrate and nitrite. The HPIC analysis was also set up to measure NH_4^+ but this was only detected in the three interstitial water samples and was below detection limits in all other samples. The concentrations of NH_4 ranged from 31 to 86 mg/L in the interstitial water samples and was in all cases higher than the concentration of K. High NH_4 concentrations in interstitial waters, such as those measured in the De Hoop samples, have been reported in a number of other studies and can be expected where organic matter decay takes place under anaerobic conditions (Wetzel, 1983). This is because ammonia is generated by heterotrophic bacteria as a primary end product of decomposition of organic matter and is present primarily as NH_4^+ in interstitial waters (Wetzel, 1983).

Recent nitrogen levels in the inflow waters at the top of the vlei, and at two stations in the vlei water have been monitored by PD Toens and Associates (1996). Their data are presented in Appendix 4. They found that both nitrate and ammonium showed periodic increases following high rainfall and inflow to the vlei from the catchment. Because of this they attributed nitrogen increases to fertilizer contamination. Their analyses had detection limits of 0.1 mg/L so they were only able to measure periodic increases above this value.

While periodic increases in N could be the result of fertilizer contamination it is not proof of such contamination. There is no evidence that the levels in influent waters following rainfall, which are higher than those in the vlei, are not the natural catchment levels. A decrease of N in the vlei water following inputs from the catchment is to be expected and has been measured in a similar environment (Hark, 1994). A gradual loss of N from the vlei water, which would result in the observed pattern of N concentrations over time, can be attributed to denitrification in the vlei sediments.

PD Toens also performed a linear fit on nitrogen levels against time using the DWAF data, in order to investigate whether N levels have increased in recent times. This shows a slight decrease in N concentration over time but is unreliable as the regression is not statistically significant.

3.4.5.2 Phosphorus

Results of P analyses on all water samples are given in Table 3.5. These results indicate large differences in the concentrations of dissolved P between the waters of the catchment and those of the vlei. Surface waters of the catchment collected during the first sampling period varied between 0.05 and 2.75 mg/L while all vlei samples were below 0.04 mg/L. This would

Table 3.5 Phosphorus, fluoride and silicon concentrations of water samples. All values are in mg/L. Blank values indicate where analyses were not done. (bdl = below detection limits) Detection limit for P = 0.01 mg/L.

Sample	P	F	Si
M3	0.02	0.7	0.17
M5	0.03	0.9	0.18
M5-2	0.04		0.02
M6	0.01	0.8	0.15
M9	0.04	0.9	0.24
D3-2	0.05		
D4-2	0.06		
H1	0.01	0.3	0.38
H1-2	0.60		
H4	0.01	0.2	0.96
T1	bdl	0.1	3.52
T2	bdl	0.1	3.22
T3	0.02	0.1	5.66
T7-2	0.03		0.05
W3-2	0.32		2.90
W2-2	0.29		
P1	0.09	0.4	0.36
P2	0.05	0.2	2.62
P3	0.45	0.2	
P4	0.36	0.3	0.25
S4-2	0.39		
S1	2.75	0.3	1.40
S1-2	0.48		
S2	0.17	0.6	4.09
S3	0.90	0.5	1.97
DF	0.01	0.1	8.55
IM3-100	1.21		4.27
IM5-150	1.13		5.11
IT2-210	0.09		11.70

seem to indicate that P is being removed from the water column in the vlei. An examination of waters from the second sampling which were collected from the top end of the vlei support this. The group of samples S1-2, S4-2, W2-2, and W3-2 was collected along a southward traverse in the lower part of the Sout River and upper part of the vlei. There is a steady increase in the EC southwards, probably due to increasing evaporative concentration, but there is a corresponding, steady decrease in the P concentration. The vlei waters further south all have much lower P concentrations with the exception of sample H1-2. Loss of P from the water column could be explained by precipitation of P minerals. According to the classification of trophic status by P concentration of Lewis *et al.* (1984) described in section 2.4.5, the De Hoop Vlei would be classified as eutrophic. The supersaturation of the water with respect to P minerals is discussed in the next section.

Concentrations of P from the DWAF data show a variation from less than 0.005 to 0.48 mg/L. The average value of P in the vlei is 0.09 mg/L but considerably higher peak values occur from time to time. Such a pattern of P levels has been measured in Lake Dillon in the U.S.A. (Lewis *et al.*, 1984) and is consistent with introductions of high levels of P from contamination in influent rivers followed by a process of depletion in the water column of the lake. From the available data, there is, however, no proof that the peak values are the result of contamination rather than the result of natural processes. The average value of P at the Kykoedy monitoring station on the Sout River is 0.07 mg/L, which is lower than that in the vlei. At Kykoedy, however, peak values of up to 0.80 mg/L occur. It should be noted that Kykoedy is some distance up the Sout River from the vlei. There is, therefore, potential for input of P between Kykoedy and the vlei. In this study, a higher P concentration was measured in sample S1, which was collected some distance downstream of Kykoedy, than in the sample from Kykoedy.

The concentration of P in interstitial waters is far higher than in the overlying bulk waters in all cases (see Table 3.5). Such a condition has been reported in a number of other studies (Lewis *et al.*, 1984; Knesl, 1996). Lewis attributed this to decomposition of organic matter liberating P in the sediments. Another factor which could play a role is the effect of the lower pH of interstitial waters on the solubility of solid phases of P present in the sediments.

Recent P levels in the inflow waters at the top of the vlei, and at two stations in the vlei, have been monitored by PD Toens and Associates (1996). These data are given in Appendix 3. The levels of P showed similar behaviour to N, with periodic increases following high rainfall and inflow to the vlei from the catchment. Increases in P were again attributed to fertilizer contamination. As in the case of N discussed above, this is, however, not proof of

contamination. Detection limits were the same as those for nitrogen levels. The linear fit on P levels against time, using the DWAF data, showed a slight increase over time but was also unreliable as the regression was not statistically significant. Higher than normal P values have been measured by PD Toens and Associates in some months where no inflow has occurred. They have stated that the reason for these increases is unknown. These may, however, be the result of a movement of P from the interstitial waters, which contain high levels of P, to the bulk waters. Such a process may also be the reason for the high P values measured in sample H1-2 in the present study.

3.4.6 Minor and trace elements

The waters of De Hoop Vlei are characterised by high pH values and high carbonate and phosphate concentrations. Under such conditions the concentrations of trace metals in the water would be expected to be low due to the low solubility of most carbonates and phosphates of such metals at high pH. Low concentrations in the water samples gave rise to analytical problems. The initial results obtained using ICP-AES in the first set of water samples were well in excess of expected values based on comparable saline, alkaline waters (eg. Last, 1993). Repeated analyses on a different instrument, with lower detection limits, produced results which were more consistent with expected values. It is these results which are, therefore, presented and used for discussion. Of the trace elements, only Si showed agreement between the two analytical runs. The Si results for samples analyzed in the first run were, therefore, retained and are presented in Table 3.5. Fluoride concentrations, determined using an ion selective electrode, are also given in this table.

Silicon is removed from the water column of lakes through adsorption, precipitation or biological uptake by diatoms which are capable of accumulating large quantities of Si (Wetzel, 1983). From the results in Table 3.5 it is evident that Si is being removed from the water column in De Hoop Vlei. Measured Si concentrations in De Hoop are lower in the southern part of the vlei than in the northern parts of the vlei and the catchment. This is despite a higher pH in the southern part and an increase in SiO_2 solubility with increasing pH. Removal of Si from the water column could, however, occur through precipitation of silicate minerals other than quartz. In the following section it is shown that the waters are supersaturated with respect to sepiolite. This mineral decreases in solubility with increasing pH and its precipitation could, therefore, explain Si loss from the water column. Silicon could also be removed from the water column by biological uptake.

Silicon concentrations in groundwater samples and those influenced by groundwaters are far

higher than other vlei waters. This is likely to be partly due to the long residence time of groundwaters which are, therefore, able to equilibrate with quartz and other silicate minerals. The silicon concentration of interstitial waters is also very high in comparison to the bulk waters. Wetzel (1983) states that this is a common situation in lake sediments.

The concentration of fluoride in the samples ranges from 0.1 to 0.9 mg/L with higher values in the De Mond waters than in the waters of the catchment. The lowest values occur in the spring waters and the groundwater sample. Fluoride concentrations in the DWAF data range between 0.4 and 1.3 mg/L.

Results of the repeat of ICP-AES analyses of transition metals in a few water samples are given in Table 3.6. Concentrations of these elements are generally low in comparison to averages for world surface waters as given by Drever (1988). Geochemical environments similar to De Hoop have been recognised as major sinks for many heavy metals (Graham, 1997). The concentrations of Ni, Cu and Zn were below detection limits in some samples while Pb was below detection limits in all samples. This is probably due to the low solubility of Pb under alkaline conditions (Alloway, 1995). The solubility of both Fe and Mn are strongly influenced by redox conditions and it would be expected that higher concentrations of these elements would occur in the more reduced interstitial waters. Sample IT2-210 is strongly enriched in Fe relative to other samples and also has the highest Mn concentration. Some precipitation occurred in the sample bottle after extraction and filtration of this water sample. This sample was, however, re-filtered immediately prior to ICP-AES analysis in order to remove this precipitation.

Table 3.6 Concentrations of trace metals in selected samples. All values are in mg/L. (bdl = below detection limits) Detection limits are as follows: Ni = 5.5 µg/L; Cu = 2 µg/L; Zn = 0.9 µg/L; Pb = 14 µg/L.

Sample	Fe	Mn	Al	Ni	Cu	Zn	Pb
M6	0.025	0.011	0.035	bdl	bdl	0.010	bdl
S1	0.032	0.035	0.019	bdl	bdl	bdl	bdl
IM3-100	0.085	0.026	0.071	0.023	0.016	0.063	bdl
IM5-150	0.042	0.011	0.017	0.018	0.007	bdl	bdl
IT2-210	2.230	0.531	0.008	bdl	bdl	bdl	bdl

The predicted speciation of minor and trace elements in the De Hoop waters was determined using the modelling programme MINTEQA2. The results of the speciation are given in Table 3.7. The speciation of trace metals in natural waters is particularly important because the bioavailability of an element is dependent on its speciation. Cotter-Howells *et al.* (1997) state that there is a consensus of opinion that bioavailability (and hence toxicity) is chemically correlated with free metal ion concentrations, although there is no definitive proof. In this regard it is interesting to note that Ni, Cu, Zn and Al all occur almost entirely in species other than their free ions at the measured concentrations in De Hoop Vlei. In the alkaline conditions, hydroxide and particularly carbonate complexes predominate. Carbonate complexes are the predominant forms of Ni, Cu and Zn, and Al forms mainly $Al(OH)_4^-$ at the pH values prevalent in the De Hoop waters. Of these metals the only one occurring as a free ion is a small percentage of Zn in one of the samples. On the other hand, Fe^{2+} and Mn^{2+} occur predominantly as the free ion with $FeOH^+$ becoming an important species at higher pH (sample M6). The behaviour of some of these metals at higher concentrations is considered in section 3.4.11.

Silica occurs predominantly as H_4SiO_4 in samples S1 and IM3 but in sample M6 which has a higher pH, $H_3SiO_4^-$ becomes the dominant form and an additional species, $H_2SiO_4^{2-}$, occurs in small amounts. Fluorine occurs predominantly as the free ion but MgF^+ also occurs and, at higher pH, a small amount of NaF^0 is predicted to occur.

3.4.7 Mineral saturation

The geochemistry of waters may be understood in terms of thermodynamic principles. Using these principles, saturation indices may be calculated for possible solid phases which may control the concentrations of dissolved constituents (Nordstrom and Munoz, 1994). A positive saturation index for a particular mineral in water indicates that the water is supersaturated with respect to the particular mineral and that it is thermodynamically possible for that mineral to precipitate. A negative saturation index, on the other hand, indicates that the water is undersaturated with respect to the particular mineral. Water that is in equilibrium with a solid phase will have a saturation index of zero. If a certain mineral is controlling the concentration of dissolved species in the water column, therefore, the water is likely to have a saturation index close to zero for that mineral. If saturation indices are much greater than zero, it is likely that the particular mineral is not precipitating for some reason and, therefore, not controlling dissolved concentrations. While saturation indices indicate thermodynamic controls on precipitation, they indicate nothing about kinetic controls (Nordstrom and Munoz, 1994).

Table 3.7 Predicted speciation of minor and trace elements in selected samples using MINTEQA2. Values are given as % of the total concentration used as input to the speciation programme.

Input species	Predicted species	M6	S1	IM3
H_4SiO_4	H_4SiO_4	45.7	91.6	97.3
	$H_3SiO_4^-$	52.4	8.4	2.7
	$H_2SiO_4^{2-}$	1.9		
F^-	F^-	75.3	79.8	
	MgF^+	23.3	19.1	
	NaF^0	1.2		
Fe^{2+}	Fe^{2+}	53.2	88.7	94.7
	$FeOH^+$	41.5	6.5	1.7
	$FeSO_4^0$	3.1	3.9	3.3
	$FeOH_2^0$	1.6		
Mn^{2+}	Mn^{2+}	71.9	79.3	71.0
	$MnCl^+$	17.9	13.4	17.6
	$MnOH^+$	4.6		
	$MnSO_4^0$	4.3	3.6	2.6
	$MnHCO_3^+$		3.0	8.1
Al^{3+}	$Al(OH)_4^-$	99.9	98.7	95.9
	$Al(OH)_3^0$		1.3	4.1
Ni^{2+}	$NiCO_3^0$	23.1	57.5	52.6
	$Ni(CO_3)^{2-}$	76.8	42.2	46.9
Cu^{2+}	$CuCO_3^0$			40.9
	$Cu(CO_3)_2^{2-}$			26.4
	$Cu(OH)_2^0$			31.5
Zn^{2+}	Zn^{2+}			1.3
	$ZnCO_3^0$	2.1		8.1
	$Zn(CO_3)_2^{2-}$	84.9		88.8
	$Zn(OH)_2^0$	11.6		

The geochemical model MINTEQA2 was used to assess the levels of mineral saturation in the water samples. Saturation indices for various minerals were calculated using the model. Input components used for the calculations on all samples were pH, major cations and anions (with total carbonate as CO_3), PO_4 and Si. The calculated saturation indices for various minerals containing these components are presented in Table 3.8. On some samples, the additional trace elements Al, F, Fe, Mn, Cu, Ni and Zn were input to the model. The saturation indices of some additional minerals containing these elements are presented in Table 3.9. Both Al and Si were measured using ICP and so values obtained may be higher than actual dissolved concentrations due to the possible presence of suspended particulate matter finer than the filters (0.2 μm) used for sample clean-up. Actual saturation indices for Al and Si minerals may, therefore, be lower than the calculated values.

The water samples shown in Table 3.8 were chosen to represent the different types of water composition occurring in the set of water samples. Two samples from the DWAF database were also chosen. These samples represent the first and last in a concentration series from July 1990 to April 1991, a period during which no significant rainfall occurred and the water was steadily concentrated by evaporation. Over this period the EC increased from 737 to 1470 mS/m. The pH of the July 1990 sample was 8.9 and that of the April 1991 sample was 9.5.

All water samples in Table 3.8 were supersaturated with respect to calcite, aragonite and dolomite, with dolomite saturation being higher than that of calcite and aragonite. Dolomite saturation increases with evaporative concentration to an extent which suggests that dolomite precipitation is not occurring. The saturation indices of calcite and aragonite are in the range which suggests that they could be playing a role in controlling concentrations of dissolved Ca and carbonates. Equilibrium with calcite would be expected in sample T1 which is a groundwater from a limestone environment. This sample is closest to having a zero saturation index for calcite. The saturation index of monohydrocalcite, which is slightly more soluble than calcite and was identified as a secondary precipitate in De Hoop Vlei (see Chapter 4), is positive and very close to zero in all samples except T1. Precipitation of monohydrocalcite could, therefore, be expected. The other secondary precipitate identified was nesquehonite. The saturation index for this mineral was negative in all the samples but it was almost zero in sample M6 which is located close to where the mineral was identified in secondary precipitates. Sample M5-2 (not shown in Table 3.8) had a saturation index of + 0.03 with respect to nesquehonite. Precipitation of nesquehonite is also, therefore, thermodynamically feasible.

Table 3.8. Saturation indices for a selection of minerals calculated on water samples using MINTEQA2. The Jul 90 and Apr 91 samples are from the DWAF data and represent the first and last in a concentration series from July 1990 to April 1991.

Mineral name	Formula	M6	T1	IM3	S1	Jul 90	Apr 91
Carbonates							
calcite	$CaCO_3$	1.40	0.60	1.62	1.25	1.10	1.51
aragonite	$CaCO_3$	1.27	0.46	1.48	1.11	0.96	1.37
dolomite	$CaMg(CO_3)_2$	4.29	0.62	4.20	3.44	2.86	3.85
monohydrocalcite	$CaCO_3.H_2O$	0.47	-0.34	0.68	0.32	0.17	0.58
nesquehonite	$MgCO_3.3H_2O$	-0.03	-2.89	-0.33	-0.72	-1.15	-0.58
magnesite	$MgCO_3$	2.39	-0.48	2.09	1.69	1.27	1.84
hydromagnesite	$Mg_5(CO_3)_4(OH)_2.4H_2O$	3.50	-12.8	-0.67	-1.54	-3.10	0.57
huntite	$Mg_3Ca(CO_3)_4$	5.98	-3.43	5.28	3.73	2.31	4.43
Silicates							
chrysotile	$Mg_3Si_2O_5(OH)_4$	8.56	-2.87	3.30	4.35	1.79	8.18
diopside	$CaMg(SiO_3)_2$	2.13	-2.31	0.34	0.71	-1.70	3.15
sepiolite	$Mg_4Si_6O_{15}(OH)_2.6H_2O$	1.94	-2.88	1.43	1.24	-2.92	3.21
talc	$Mg_3Si_4O_{10}(OH)_2$	6.53	-1.55	4.87	4.85	-0.66	7.97
quartz	SiO_2	-1.58	0.10	0.22	-0.31	-1.79	0.67
phosphates							
hydroxy-apatite	$Ca_5(PO_4)_3(OH)$	2.24	-0.02	8.43	10.2	5.06	7.29
Sulphates							
gypsum	$CaSO_4.2H_2O$	-1.81	-2.06	-1.20	-1.57	-1.38	-1.43

Supersaturation was also predicted with respect to a number of other Mg carbonate minerals, particularly in the De Mond water. Sample M6, which has the highest Mg:Ca ratio (25.7), has the highest degree of saturation with respect to Mg carbonate minerals. The saturation indices for Mg carbonates reach fairly high values in this water, which may indicate that precipitation is not occurring. The sample with lowest Mg:Ca ratio (T1 = 0.23) is undersaturated with respect to all Mg carbonates. The saturation of all carbonate minerals in Table 3.8 increases with concentration from the July 1990 sample to the April 1991 sample and from the

catchment (S1) and spring (T1) waters to the more evolved waters at De Mond (M6).

The waters show similar patterns of saturation with respect to Ca and Mg silicates as they do with respect to carbonates. Sample M6 is supersaturated with respect to a number of silicate minerals while T1 is undersaturated with respect to all of them. Of these minerals, sepiolite is the one indicated by the saturation indices to be most likely (value closest to zero) to influence Mg concentrations in the water column.

All the waters in Table 3.8 are strongly supersaturated with respect to hydroxy-apatite. The high values of the saturation index indicate that this mineral is, however, probably not precipitating in the vlei. Highest saturation indices occur where P concentrations are high. The saturation index also increases in the concentration series from July 1990 to April 1991. Saturation indices for an F substituted apatite (Table 3.9) were even higher than those for hydroxy-apatite.

Because of the high ammonium and phosphate levels present in the interstitial water samples it was thought that the mineral struvite ($NH_4MgPO_4.6H_2O$) could be supersaturated and influence phosphate solubility in the vlei. This mineral is not accounted for in the MINTEQA2 data base. Its saturation index was, therefore, calculated from the relevant ion activities obtained from the MINTEQA2 output, using the dissolution reaction

$$NH_4MgPO_4.6H_2O + 2H^+ \rightleftharpoons Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2O$$

and a log K value of 6.40 (Vieillard and Tardy, 1984). These calculations, however, showed that the interstitial waters were undersaturated with respect to struvite.

The bulk vlei samples and catchment samples are not supersaturated with respect to quartz, but the spring water and interstitial waters are. All water samples are undersaturated with respect to gypsum and it is, therefore, not likely to precipitate in De Hoop Vlei. The catchment and interstitial waters are supersaturated with respect to a number of alumino-silicate minerals but the De Mond water is not. This is probably a result of the lower Si concentrations and higher pH at De Mond.

Table 3.9 gives the saturation indices for those minerals containing Mn, Cu, Zn and Ni, which are closest to zero. Water samples IM3 and S1 are supersaturated with respect to the mineral $MnHPO_4$ probably due to the high P concentrations in these waters. The other positive saturation index occurs for $ZnSiO_3$ in both samples in which Zn was measured. At the low

concentrations at which they occur in De Hoop Vlei, the waters are undersaturated with respect to all other solid phases of these elements. Trace metals are, however, not only precipitated in pure solid phases but often co-precipitate with other minerals and are adsorbed on mineral surfaces, particularly on iron oxide coatings (Hamilton-Taylor and Davison, 1995). Furthermore, the potential for these metals to form or to be incorporated in sulphide minerals, under reducing conditions, was not considered in the MINTEQA2 calculations.

Table 3.9 Saturation indices for a selection of minerals calculated on water samples using MINTEQA2.

Mineral name	Formula	M6	IM3	S1
kaolinite	$Al_2Si_2O_5(OH)_4$	-2.57	4.84	1.59
muscovite	$KAl_2Si_3AlO_{10}(OH)_2$	-1.36	8.40	3.72
FCO_3 apatite		9.80		23.2
	$MnHPO_4$	-2.82	0.42	1.14
rhodochrosite	$MnCO_3$	-0.30	-0.54	-0.29
tenorite	CuO		-1.00	
	$ZnSiO_3$	0.67	1.22	
	$ZnCO_3.H_2O$	-3.51	-2.11	
	$Ni(OH)_2$	-2.50	-4.02	-4.27

3.4.8 Brine evolution and solute behaviour during evaporative concentration

The behaviour of different solutes during evaporative concentration in closed basins has been discussed in section 2.4.2. The behaviour of a particular solute is indicated by plotting its concentration against a suitable measure of evaporative concentration. This gives an indication of the extent to which the solute is controlled by evaporation. The chloride concentration is commonly used as such a measure of evaporative concentration because chloride is not known to be removed from solution until halite saturation is reached (Kilham and Cloke, 1990).

Figure 3.4 plots the concentrations of the major ions against chloride concentration for the DWAF data from De Hoop Vlei. A 1:1 line is plotted on each graph to indicate deviation from conservative behaviour and to facilitate comparisons between the different graphs. The plot of Na indicates that its behaviour is close to being conservative in De Hoop Vlei while

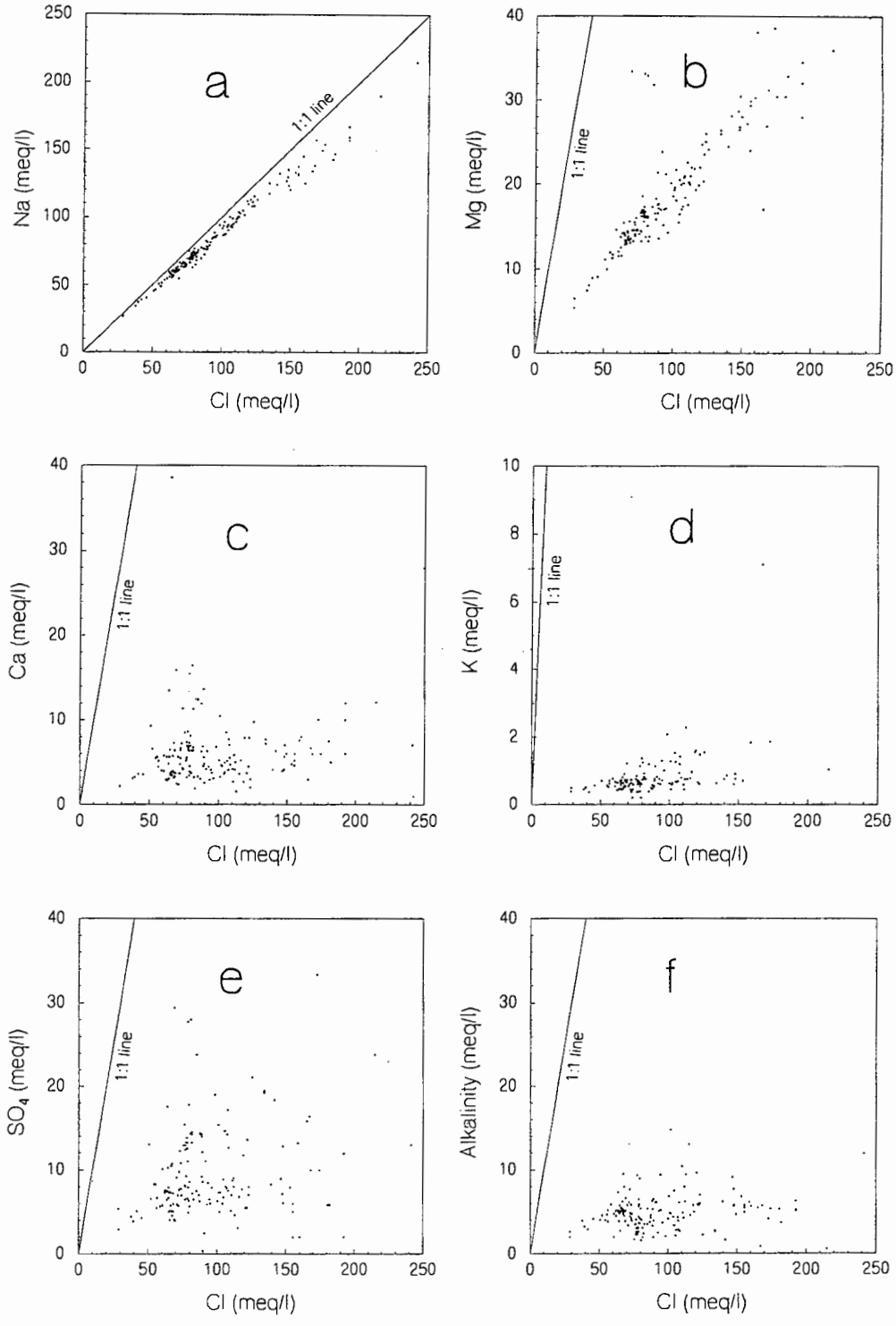

Figure 3.4 Plots of the concentrations of all major ions against chloride concentration for the DWAF data from De Hoop Vlei.

all other major ions deviate significantly from conservative behaviour. This indicates that all the major ions are being lost from the water column, relative to chloride, during evaporative concentration.

Although the plot of Na indicates that its behaviour is close to being conservative, the slope of the regression line is slightly less than the 1:1 line, which indicates that a small amount of Na is lost relative to chloride. Such a condition is unusual and many authors have instead recorded conservative behaviour for Na in saline lakes (Hammer, 1986; Drever, 1988; Evans and Prepas, 1996; Knesl, 1996). A mechanism which could explain Na loss relative to chloride is exchange of Na for other cations on exchange sites in the sediments. Because Na is the most weakly adsorbed of the major cations, significant Na adsorption as evaporative concentration takes place would not be expected, unless there is some mechanism by which other cations are stripped off exchange sites on clay minerals in the sediments. The precipitation of Ca and Mg as carbonates could conceivably bring about the vacation of adsorption sites occupied by Ca and Mg, making it possible for Na to occupy clay surfaces.

Magnesium shows a loss relative to chloride over the whole concentration range but the slope of the regression line is significantly less than the 1:1 line indicating a greater loss of Mg than Na. This behaviour is consistent with Mg being precipitated from the water column. The presence of a Mg carbonate, nesquehonite, was detected in secondary precipitates (see section 4.4.7.3). Both the more dilute waters of De Hoop and those that have been concentrated are supersaturated with respect to a number of other Mg carbonate and silicate minerals. Precipitation of these minerals is, therefore, possible.

The Ca data show a high degree of scatter and a high loss of Ca relative to chloride. All the De Hoop waters are supersaturated with respect to $CaCO_3$ minerals and precipitation of $CaCO_3$ is, therefore, likely. A depletion of Ca following $CaCO_3$ precipitation (type IIb behaviour as identified by Eugster and Jones (1979) and discussed in Chapter 2) is anticipated since the equivalent concentration of Ca is lower than that of alkalinity in the water. The high degree of scatter in the data may be explained by the different composition of input waters and the introduction of different levels of Ca due to mixing of these waters. Such a process has been identified as probably influencing Ca concentrations in the samples collected for this study (see section 3.4.3.1).

Potassium depletion is the most pronounced of all the major ions relative to Cl. This indicates a very effective removal of K, probably by uptake in clay minerals. Mica minerals are the dominant clay minerals in the De Hoop sediments. Many authors have suggested that K is

lost from solution in African lakes containing illite-rich sediments (Kilham and Cloke, 1990). Weathering of the edges of primary mica minerals, which is common in illites, would allow for the preferential uptake of K (McBride, 1994) and, therefore, its effective removal from solution.

The behaviour of both of the monovalent ions, Na and K, in De Hoop Vlei is different to their behaviour in Barbers Pan, a sub-saline, alkaline pan in South Africa, which is geochemically similar to De Hoop Vlei. In Barbers Pan Na shows conservative behaviour and K depletion is less pronounced than in De Hoop Vlei (Knesl, 1996). The stripping of divalent cations from exchange sites, posed above as a possible explanation for the non-conservative behaviour of Na in De Hoop Vlei, may also facilitate the effective uptake of K. The observed differences between De Hoop Vlei and Barbers Pan in terms of the behaviour of Na and K may be explained by the hypothesis that De Hoop provides a higher potential for the stripping of divalent cations from exchange sites than occurs in Barbers Pan. The higher potential may be the result of more regular and greater introductions of clay rich sediment into the vlei than into Barbers Pan. These clays are likely to have a high exchangeable divalent ion percentage and divalent ions could, therefore, be exchanged with monovalent ions in the vlei waters from which Ca and Mg have precipitated. The evolved waters of De Hoop Vlei have a lower divalent ions/monovalent ions ratio than the bulk water of Barbers Pan which would facilitate a greater exchange at De Hoop. Furthermore, De Hoop Vlei is shallower and would therefore provide more intimate contact between water and sediments than occurs in Barbers Pan.

Sulphate in De Hoop Vlei is also lost from solution to a fairly large extent with evaporative concentration. Because of the undersaturation of the De Hoop waters with respect to gypsum, it is more likely that SO_4 is lost through reduction to sulphides in the sediments. Sulphide minerals have been identified in the De Hoop sediments (see section 4.4.3). Some may also be lost to the atmosphere in the form of S containing gases (largely H_2S) following the reduction of sulphate through biological activity (Wetzel, 1983). The alkalinity data show a high degree of scatter. This can be explained by the number of different processes that affect the concentration of alkalinity (carbonate precipitation, biological oxidation of organic matter, degassing of CO_2 and mixing of different inflow waters).

The plots of Si and F concentrations versus Cl are given in Figure 3.5. Both show a considerable amount of scatter and there is no statistically significant correlation in the plots. The lack of correlation between Si and Cl concentrations could be explained by the removal of Si from the water column by diatoms. The specific adsorption of F on clay minerals and its adsorption on $CaCO_3$ could account for its removal from the water column. The De Hoop

waters were identified as being supersaturated with respect to a F and CO_3 substituted apatite. Precipitation of this mineral could, therefore, also be responsible for removal of F from the waters.

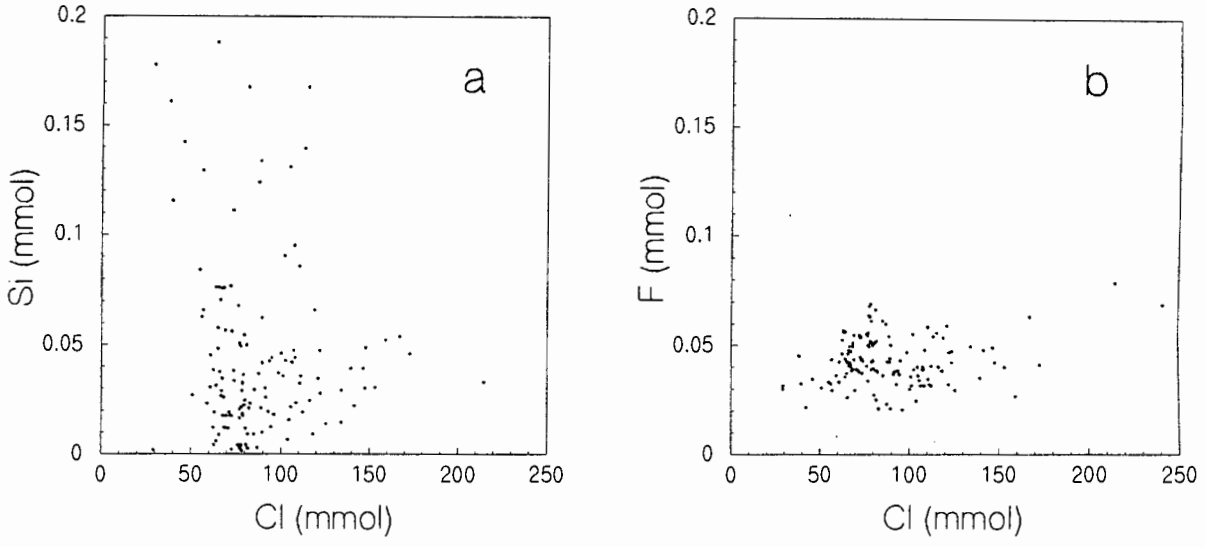

Figure 3.5 Plots of the Si and F concentrations against chloride concentrations for the DWAF data from De Hoop Vlei.

Identification of the behaviour type, as identified by Eugster and Jones (1979), that is applicable to each solute, is difficult from the data available, since the concentration range is limited. Trends that may appear at higher evaporative concentration, and reveal the solute type, are not evident. From the available data it is only possible to identify a loss of a solute from the water column during evaporative concentration.

The evolution of the De Hoop Vlei water is likely to follow path 1 of the Hardie-Eugster model during $CaCO_3$ precipitation. This is because the equivalent concentration of carbonate is greater than that of Ca in the waters. Magnesium precipitation should follow, which in the model occurs as sepiolite, but is more likely, according to Drever (1988), to be dolomite or high Mg calcite in natural environments. The available data do not cover a sufficient extent of evaporative concentration to show evidence of subsequent steps in the evolution of the brine. The next path followed by the De Hoop water is likely to be path IV of the model since the concentration of Mg is greater than that of alkalinity. The dominance of Na and Cl in the in-flow waters will affect the composition of the brine, resulting in a high degree of Na and Cl dominance.

3.4.9 Other processes which could affect water chemistry in De Hoop Vlei

3.4.9.1 Estuarine mixing processes

The mixing of waters of different salinities, which commonly occurs in estuaries and can also take place in saline lakes, can influence the chemical composition of the water (Burton, 1976). Salinity stratification or density stratification can also occur where less saline water flows into water with a higher salinity. In De Hoop Vlei the inflow water from the Sout River has a similar salinity to the vlei water and the potential for these processes to occur is, therefore, limited. At times of high inflow during rains the salinity difference may, however, be sufficient. Furthermore, the Tierhoek spring water and the vlei water have different salinities and mixing and stratification processes may play a role when these waters come into contact.

3.4.9.2 Water stratification

Other studies have indicated that thermal water stratification does not occur at De Hoop to any significant extent (Coetzee, 1986). This would be expected, given the shallow water depths and high incidence of windy conditions. Water temperature throughout the water column is, therefore, likely to be closely related to air temperature (Hammer, 1986). Water stratification was consequently not taken into account for sampling purposes.

3.4.9.3 Differential dissolution of efflorescent crusts

The differential dissolution of efflorescent crusts is a process which can affect the chemical composition of saline lakes subjected to cyclic wetting and drying (Drever, 1988). Sparingly soluble salts, precipitated during evaporative concentration, do not undergo re-dissolution following wetting as readily as do more soluble ones. This results in differential dissolution, and enrichment of the water in the components of the more soluble salts. If the lake dries out again before dissolution of the sparingly soluble salts, they remain in the solid phase. The net effect over time is to deplete the water of the ions comprising these salts.

Although De Hoop vlei is subjected to cyclic wetting and drying and efflorescent crusts are likely to form in areas which are completely desiccated, this process is unlikely to greatly influence the water chemistry. This is because complete drying of the vlei is infrequent and the vlei usually holds water for a long period of time following renewed inflow to the vlei. This means that sparingly soluble salts of efflorescent crusts would have sufficient time for dissolution in the lower salinity water. Drever (1988) states that waters influenced by

differential dissolution should be strongly undersaturated with respect to gypsum and sepiolite. The waters of De Hoop that are subjected to evaporative concentration are, however, supersaturated with respect to sepiolite. They are undersaturated with respect to gypsum but this is more likely to be as a result of loss of sulphate through other processes.

3.4.10 Water quality for different uses

The water of De Hoop Vlei has a naturally high salinity which precludes its use as a water resource for human use. The TDS is far in excess of stipulated standards for domestic, irrigation and livestock use (Department of Water Affairs and Forestry, 1993). The pH of some of the waters is also in excess of these standards (>pH 9). No minor or trace elements are, however, in excess of the standards.

The waters of the Tierhoek spring are of a quality suitable for domestic use. The EC of these waters is above the target guideline of 70 mS/m but this only imparts a salty taste and has no health implications. All other parameters for this water, which were measured in this study, are within the recommended standards. Borehole water of similar origin and quality is used for domestic purposes in the De Hoop Nature Reserve. The water is, however, hard and supersaturation with respect to $CaCO_3$ minerals may result in the build-up of precipitates of these minerals in water pipes (Snoeyink and Jenkins, 1980).

It should be noted that, because of the nature of the De Hoop Vlei, the consideration of its water quality from a human-use perspective is not as important as its quality for the natural biota. These are adapted to the natural water quality but may be affected by changes in water quality brought about by human activities.

3.4.11 Modelling pollution in De Hoop Vlei

By making use of geochemical modelling, it is possible to predict equilibrium concentrations of certain pollutants in the vlei water in response to increased loading of input waters. Such a modelling approach has been used recently by Rawlins *et al.* (1997) in an investigation of Welsh streamwaters. Theoretically, the concentration of trace metals should not greatly exceed a concentration at which the water becomes supersaturated with respect to a particular solid phase of that metal (Nordstrom and Munoz, 1994).

The geochemical modelling programme MINTEQA2 was used to predict the result of hypothetical increases in Zn and Pb concentrations in the waters of De Hoop Vlei. These

metals could conceivably be introduced as pollutants to the vlei. Both have been identified as contaminants in Norwegian lakes from long-transported pollution (Larsen *et al.*, 1996). Zinc is furthermore a constituent of fertilizers used in the De Hoop catchment (Pers. comm., F. Goosen).

The modelling was done by investigating saturation indices of different Zn and Pb minerals at different dissolved metal concentrations. The calculated saturation indices are presented in Table 3.10. The water composition used for the modelling was that of the DWAF sample from July 1990. This water was chosen as one of moderate salinity, typical of the water composition following inputs of water to the vlei from the Sout River. In the vlei waters which have become concentrated by evaporation, the equilibrium concentrations of Pb and Zn are likely to be lower.

Table 3.10 Saturation indices, calculated using MINTEQA2, for Pb and Zn minerals in the De Hoop water at different hypothetical input concentrations of Pb and Zn. The water composition is that of DWAF sample from July 1990.

Metal concentration	Saturation index		
	pyromorphite		cerussite
Pb	$(Pb_5(PO_4)_3Cl)$	$(Pb(OH)_2)$	$(PbCO_3)$
0.02	-0.12	-0.62	-1.29
0.04	1.39	-0.32	-0.99
0.08	2.90	-0.02	-0.69
0.20	4.89	0.38	-0.29
		willemite	zincite
Zn	$(ZnSiO_3.H_2O)$	(Zn_2SiO_4)	(ZnO)
0.00	0.04	-3.60	-2.38
0.2	1.64	-0.40	-0.78
0.4	1.94	0.21	-0.47
0.8	2.25	0.82	-0.17

The results showed that, at Pb concentrations below 0.02 mg/L, the water was not supersaturated with respect to any Pb minerals. At a concentration of 0.04 mg/L the water is supersaturated with respect to the mineral pyromorphite $(Pb_5(PO_4)_3Cl)$. Precipitation of pyromorphite could, therefore, buffer the dissolved Pb concentration in the vlei water at a

value of around 0.02 mg/L and significantly higher concentrations would not be expected. If pyromorphite precipitation does not occur, Pb concentrations can increase to 0.08 mg/L, at which point the water would become supersaturated with respect to the mineral $Pb(OH)_2$, and precipitation of this mineral would be expected. The next Pb mineral closest to saturation is cerussite ($PbCO_3$), but at a dissolved Pb concentration of 0.2 mg/L the water is not yet saturated with respect to this mineral.

The saturation of the water with respect to the mineral $ZnSiO_3$ occurs at a low Zn concentration of around 0.005 mg/L. However, both sample M6 and IM3 were supersaturated with respect to this mineral (see Table 3.9) and it, therefore, appears that precipitation of $ZnSiO_3$ is not buffering the Zn concentration in the water. According to the modelling, the next Zn mineral to precipitate would be willemite (Zn_2SiO_4). Saturation of the water with respect to this mineral would occur at a Zn concentration of around 0.4 mg/L. At a concentration of 0.8 mg/L the water is close to saturation with respect to another Zn mineral, zincite (ZnO).

This modelling suggests that the waters of De Hoop Vlei are capable of effectively buffering the concentration of Pb and Zn at low levels. This buffering is likely to limit the ecological effect of an introduction of these elements as contaminants into the vlei.

3.4.12 Conclusions

The water chemistry of De Hoop Vlei is characterised by a high degree of spatial and temporal variation. In general the waters analyzed during this study were alkaline and were either saline, with Na and Cl as dominant ions, or non saline with higher proportions of dissolved Ca and carbonate. The EC of vlei water samples varied between 86 and 3070 mS/m and those from the catchment ranged between 65 and 2160 mS/m. Interstitial waters had a higher salinity than the overlying bulk waters in all cases. Highest salinity values occurred in the southern part of the vlei at De Mond, and generally decreased northwards to a minimum at the Tierhoek spring. Salinity in the influent rivers and the northern parts of the vlei was similar to the that in the south.

Spatial and temporal variation of salinity in the vlei is adequately explained by the mixing of high and low salinity inflow waters and by evaporative concentration. From the available data, there is no conclusive evidence of a general increase in salinity over time. The waters of De Hoop Vlei would generally be classified as hyposaline, having a salinity between 3 and 20 g/L, but in the southern parts of the vlei the waters become mesosaline (>20 g/L) during

dry periods. The high salinity of the water precludes its use as a water resource for human use.

The pH of the De Hoop Vlei waters is high. Sample pH varied between 7.7 and 10.0 for the vlei waters but was lower (7.5 - 8.8) for those of the catchment. Evaporative concentration and brine evolution resulted in elevated pH levels, with the highest values occurring at De Mond. The increase in pH can probably be attributed to loss of carbonates from the water column through transfer to the sediments as well as uptake during photosynthesis. The pH of interstitial waters in the sediments was between 1 and 2 pH units lower than that of the overlying bulk waters. This may result from the acidifying effects of the anaerobic oxidation of organic matter.

Although the proportions of the major ions vary considerably through the study area, Na is the dominant cation and Cl the dominant anion in all but one sample. From the major ion chemistry, it is possible to distinguish three broad types of waters in the study area: (1) water characteristic of influent waters from the Sout and Potberg rivers; (2) spring water from a limestone environment; and (3) brines evolved by evaporative concentration of influent waters. The waters differ most notably with respect to relative Ca proportions which are evident in Mg/Ca ratios. Highest Ca proportions occur in the spring waters and the lowest proportions are in the evolved brines. The cation concentration sequence changes from Na > Ca > Mg > K for the spring waters to Na > Mg > K > Ca for the brines. The majority of vlei waters have the anion sequence Cl > SO_4 > (HCO_3 + CO_3).

In all cases interstitial waters have higher Ca and carbonate proportions than the overlying bulk waters. This may be due to the higher solubility of $CaCO_3$ at the lower pH and higher CO_2 levels which would result from microbial decomposition of organic matter in the sediments.

The high salinity and NaCl dominance of all waters in the study area was considered evidence of the significant contribution of wind blown sea salts to the salinity of the De Hoop waters. The Bokkeveld shales of the catchment can also be expected to contribute significant amounts of salts to the vlei.

Nitrate and nitrite were below detection limits in all samples. Nitrogen was only detected in interstitial samples in the form of NH_4^+. The detectable ammonium concentrations in interstitial waters were explained as a product of the decomposition of organic matter in the sediments. Monitoring of N levels in the vlei and influent waters, done as part of another

study, revealed that both nitrate and ammonium showed periodic increases following high rainfall and inflow to the vlei from the catchment.

The results of P analyses indicated large differences in the concentrations of dissolved P between the waters of the catchment and those of the vlei. Surface waters of the catchment had P concentrations as high as 2.75 mg/L while all vlei waters sampled at the same time were below 0.04 mg/L. The results suggest that it is likely that P enrichment of surface waters is occurring in the catchment, although these levels may be natural. The results also show that P is effectively being removed from the water column in the vlei. The concentration of P in the interstitial waters was far higher than in the overlying bulk waters. Monitoring of P levels in the vlei and influent waters revealed that its behaviour was similar to N with periodic increases following high rainfall and inflow to the vlei from the catchment. The De Hoop Vlei may be classified as eutrophic in terms of the concentrations of P in the water.

Silicon concentrations were also lower in the southern part of the vlei than further north and were higher in interstitial waters. The loss of Si from the water column may be due to uptake by diatoms and to precipitation of silicate minerals such as sepiolite. Concentrations of trace metals were extremely low, as was expected due to the high pH and high carbonate content of the system. The predicted speciation of trace metals, excluding Fe and Mn, showed that they are likely to occur almost entirely in species other than their free ions. Under the prevailing alkaline conditions, hydroxide and particularly carbonate species predominate. The modelling results of pollution inputs into the vlei water indicated that the vlei is likely to effectively buffer the concentrations of the trace metals Pb and Zn at low levels, and thereby limit environmental effects resulting from their introduction into the vlei.

Calculations using MINTEQA2 indicated that all water samples were supersaturated with respect to calcite, aragonite and dolomite. Some waters, particularly at De Mond, were also supersaturated with respect to a number of other Mg carbonate minerals. Precipitation of calcite, aragonite, monohydrocalcite, nesquehonite and sepiolite was indicated as feasible in De Hoop Vlei. The waters were also strongly supersaturated with respect to both hydroxy-apatite and a F and CO_3 substituted apatite.

During the evolution of the vlei water by evaporative concentration a small amount of Na is lost from the water column relative to chloride. This unusual behaviour of Na can possibly be explained by stripping of Ca and Mg from exchange sites due to their precipitation as carbonates, which enables Na to exchange for these cations on exchange sites in the sediments. The other major solutes are all removed from the water column to a significant

extent during evaporative concentration. The stripping of divalent cations from exchange sites may also facilitate the effective uptake of K during evaporative concentration and explain the extent of its removal from the water column. The evolution of the De Hoop water is likely to follow path 1 of the Hardie-Eugster model during $CaCO_3$ precipitation because the equivalent concentration of alkalinity is higher than that of Ca. This means that the Ca concentration will become very small with increased evaporative concentration.

Chapter 4 Geochemistry of the sediments of De Hoop Vlei

4.1 Introduction

Sediments play an important role in the biogeochemical cycling of elements and there is a continual transfer of elements between the sediments and the water column of lakes (Wetzel, 1983). In order to understand the factors that affect the water chemistry of De Hoop Vlei, therefore, it is essential to have information on the geochemical characteristics of the sediments. The sediments of De Hoop Vlei have never previously been investigated in any detail.

The objective of this chapter is, therefore, to provide a geochemical characterization of the sediments of De Hoop Vlei. This characterization is based on an interpretation of the analyses of sediment samples collected during the study. The samples were taken to adequately cover the expected variation along the length of the vlei. This chapter includes a description of the sampling procedures as well as the methods used for analysis. It focuses on aspects of the sediment geochemistry which are pertinent to the interaction between sediments and water chemistry in De Hoop Vlei.

4.2 Sampling

Sediment samples were taken during the same two sampling trips in which water samples were taken. These took place in 1996 from October 21 to 23 and December 10 to 12, respectively. Sediments were sampled at a total of 26 locations, many of which were the same locations at which water samples were collected. Figure 3.1 provided a map showing the position of all sampling sites. The position of each was determined using a geographical positioning system. A description and details of all sampling locations are given in Appendix 1. Single samples were collected at each site. Sediments were collected in the form of cores using PVC tubes 50 cm in length with a diameter of 60 mm. These were manually depressed into the sediments to their maximum depth and then rotated and extracted. A specially designed handle which fitted onto the top of the tube made this possible. Figure 1.4 showed the hand corer being used to collect samples in the southern part of the vlei. After extraction the cores were sealed on both sides with tight fitting plastic caps over a sheet of plastic bag to prevent any entry of air. They were kept in an upright position and frozen at -20°C in the laboratory.

In some cases where it was not possible to use the corer for sampling, grab samples were collected instead. In these cases sediments were scooped directly into plastic jars with the aid of a plastic spade if necessary and only the surface sediments to an approximate depth of 4 cm were collected.

The frozen sediment cores were extracted from the PVC tubes by cutting these open with a circular saw. Cuts were made down the length of the tube on opposite sides so that the PVC tubing could be removed from the intact length of frozen core. The cores were inspected and divided into depth sections based on their appearance due to colour and grain size differences. This was done using a jaw splitter to split the cores perpendicular to their length. The frozen sections were transferred into plastic jars. After thawing the sections were spread out on paper and air dried for a number of days. Necessary precautions were followed to prevent contamination between cores during all these procedures.

The same sample numbering conventions used for water samples and described in section 3.1.1 were also applied to sediment samples. Thus each sampling site was assigned a letter describing its general position within the study area followed by a number for the particular site. The sections of a core are distinguished by the lower depth of the section in millimetres given after the sample site number. Those samples collected as grab samples are denoted by a G following the site number.

4.3 Analytical methods

To ensure the accuracy and precision of the laboratory analyses, certain samples were analyzed in duplicate and standards were run where possible. Details of the results of these procedures and indications of the precision and accuracy of data are given in Appendix 1. Data were only used when these procedures indicated acceptable levels of error.

4.3.1 pH of oxidised and reduced sediments

The pH was measured in wet sediments which had been sealed from exposure to the atmosphere and which were black in colour. It was also measured on the same samples following exposure to the atmosphere by air drying, which resulted in a change of colour from black to light brown. Distilled water was added to 10 g of air dried sediment in a centrifuge tube to give a water to sediment ratio of 2.5. In the case of the wet sediments, water content was first calculated gravimetrically after air drying and then the additional quantity of distilled water required to give the same suspension concentration as the dried

sediments, was added. The tubes were shaken on an horizontal shaker for 1 hour. they were allowed to settle for 30 minutes and then pH was measured in the supernatant using a Crison micro pH 2001 pH meter with combined glass-calomel electrode. The pH meter was calibrated before use with buffer solutions of pH 7.02 and 4.00. The tubes were sealed and allowed to stand for a further 8 weeks after which pH measurements were repeated.

4.3.2 Organic carbon

Organic carbon was determined using the Walkley-Black Method (Walkley, 1935) following the procedure in Handbook of Standard Soil Testing Methods for Advisory Purposes (Non-Affiliated Soil Analysis Work Committee, 1990). This method makes use of the fact that organic matter in soil material may be oxidised by treatment with a hot mixture of $K_2Cr_2O_7$ and sulphuric acid, according to the equation:

$$2Cr_2O_7^{2-} + 3C + 16H^+ \rightleftharpoons 4Cr_3^+ + 3CO_2 + 8H_2O$$

After completion of this reaction, the excess dichromate is titrated with iron (II) ammonium sulphate hexahydrate. The reduced dichromate is assumed to be equivalent to the organic C present in the sample, assuming that the organic matter has an average valence of zero.

Sediment samples ground for XRFS analysis using a carbon steel Siebtechnik swing mill were used for this analysis. Potassium dichromate solution, and thereafter sulphuric acid, was added to the ground samples and allowed to cool slowly. Ortho-phosphoric acid was added to facilitate the titration reaction. The excess dichromate was titrated with iron (II) ammonium sulphate solution to the ferroin indicator end-point.

4.3.3 Carbonate

The carbonate content of the sediment samples was determined by means of the 'Karbonat-bombe' (Muller and Gastner, 1971), using the method of Birch (1981). Between 0.5 and 2 grams of ground sediment (depending on carbonate content) were reacted with 5 ml of concentrated HCl in the bomb. The reaction of calcium carbonate with HCl produces CO_2 gas. The volume of CO_2 gas is measured as a pressure change on a pressure gauge fitted to the bomb. The instrument was calibrated using known masses of pure $CaCO_3$.

4.3.4 Total element analysis by XRFS

Bulk elemental analysis of major and trace elements in the sediments was determined by X-ray fluorescence spectrometry (XRFS) using a Philips PW X'Unique II X-ray spectrometer. Due to time restrictions, both major and trace elements were analyzed on powder briquettes, rather than majors being analyzed on fusion disks. This resulted in a reduced accuracy for major elements to approximately 10 percent of the concentration determined. The accuracy is nevertheless sufficient for this study in that the results give an adequate indication of differences in major element composition. Instrumental conditions are given in Willis (1995). The elements determined are listed in Table 4.3 and 4.4.

Powder briquettes were prepared from oven dried samples (105°C) which had been ground in a carbon-steel vessel for 3 minutes using a Siebtechnik swing mill to produce a fine powder (≤70μm particle size). Briquettes were pressed from 6 g of sample with boric acid as backing using a 30 mm diameter tool steel die under 10 tons of pressure. Briquettes which showed desiccation cracks were re-made by mixing 2 g of wax with 8 g of sample before pressing.

For the purpose of summing major element percentages, the water content of the ground samples used for making briquettes was determined. This was done gravimetrically by roasting samples at 950°C for 5 hours. Corrections were made for organic matter and CO_2 loss by using previously determined organic C and CO_2 values. A factor of 1.6 was used to convert organic C to organic matter for this purpose.

4.3.5 Mineralogy by XRD

4.3.5.1 Clay fraction

This analysis involved firstly the separation of the clay fraction from the sand and silt fractions and then the X-ray diffraction analysis (XRD) of the clay fraction on a prepared glass slide. In order to separate the clay fraction, it was dispersed by mechanically shaking the sediment samples at a high pH in a Na_2CO_3 solution. After dispersion the suspension was allowed to settle under gravitation and according to Stoke's law the clay size particles (<2 μm) were siphoned off from a calculated depth below the surface. The settling and siphoning procedure was repeated to accumulate enough clay. The separated clay was then flocculated by the addition of NaCl. Thereafter it was desalinated in dialysis tubing and the suspension concentration was adjusted to 20 g/L. An aliquot of 2 ml was dried on a glass slide and used

for XRD analysis.

The analysis was done using a Philips PW 1390 X-ray diffractometer fitted with a monochromator, scintillation detector and pulse hight selector. A Cu tube operating at 40 kV and 25 mA was used and the samples were scanned through a range of 5 - 60 °2θ with a step size of 0.1 °2θ and a counting time of 1 second per step.

4.3.5.2 Whole sediment and secondary precipitates

These samples were prepared for XRD by directly pressing ground samples into an XRD sample holder using a hand-held press. The press consisted of a flat, polished steel surface and wooden handle with which pressure was applied directly to the powder sample in the holder. The sample surface was pressed against Whatman no. 1 filter paper to prevent preferential orientation of minerals at the surface. In the case of the whole sediment, samples ground for XRFS analysis using a swing mill, were used. The secondary precipitate was ground briefly using a hand-held, agate mortar and pestle before being pressed into the XRD sample holder.

4.3.6 Scanning electron microscopy (SEM)

Secondary mineral precipitates were analyzed using a Leica Stereoscan 440 scanning electron microscope in the Electron Microscopy Unit of the University of Cape Town. The sample was mounted on a sample holder and Au-Pd coated prior to analysis. The instrument was operated at an accelerating voltage of 20 kV and the samples were maintained under vacuum at between 10^{-4} and 10^{-6} torr. High-resolution morphological images were obtained from the secondary electrons emitted. Energy dispersive spectrometry was used to obtain spot semi-quantitative chemical analyses.

4.3.7 Clay percentage

Clay percentage was determined on 15 sediment samples using the hydrometer method and following the procedure in Handbook of Standard Soil Testing Methods for Advisory Purposes (Non-Affiliated Soil Analysis Work Committee, 1990). This analysis was done by the Institute for Soil, Climate and Water of the Agricultural Research Council in Pretoria.

4.3.8 Extractable P, Zn and K

Extractions were done on six air-dried sediment samples using the AMBIC method which involves the use of NH_4HCO_3-NH_4F-$(NH_4)_2$-EDTA. The method follows the procedure in Handbook of Standard Soil Testing Methods for Advisory Purposes (Non-Affiliated Soil Analysis Work Committee, 1990). This analysis was also done by the Institute for Soil, Climate and Water in Pretoria.

4.4 Results and discussion

Visual inspection of the frozen cores revealed generally dark-coloured sediment material (dark greyish brown) with darker streaks of organic matter (black). In some cores clearly visible distinctions as a result of colour or particle size differences between sections were evident. The upper sections were generally darker than lower sections with distinct transitions in some cases. Dark material in the lower sections was restricted to horizontal streaks or bands. Other cores were visibly uniform throughout their length. The cores from the Rietkloof and Windhoek areas in the north of the vlei were a lighter and more intense brown colour than those from further south. Small shells (able to pass through a 2 mm sieve) were present in many of the core sections. Undecomposed organic matter was also present in many samples with fresh vegetation occurring on the surface of some cores.

The results of the clay, organic carbon, and calcium carbonate determinations in the sediment samples are given in Table 4.1. Reference can be made to Figure 3.1 for the location of the sampling stations. The results of the analyses are discussed below.

In dividing the cores into sections based on visual appearance, cores were not divided into the same length divisions. This complicates comparisons between the sections from different cores, as some differences may be the result of the different depths within a core and, therefore, depth below the sediment surface at which they occurred.

4.4.1 Particle size

The clay content of the samples varies between 16 and 64 percent, increasing northwards along the length of the vlei. This phenomenon has already been noted by Butcher (1983). The reason given by her is that wind blown sand from the dunes to the south of the vlei contributes significant amounts of sand to the sediments in the southern parts of the vlei. This

Table 4.1 The results of organic carbon, $CaCO_3$ and clay percentage determinations on sediment samples from De Hoop Vlei. All values are in mass percent. Blank values are given where analyses were not done.

Sample	Organic C	$CaCO_3$	Clay percent
M1-90	3.0	56	16
M1-255	3.5	32	28
M1-290	2.1	47	26
M2-160	1.7	50	
M3-100	2.7	57	16
M4-135	4.0	59	
M5-150	14.3	47	
M6-70	3.0	60	
M7-160	8.7	45	
M8-160	1.7	63	
M9-120	7.1	54	20
M9-240	5.8	37	26
M10-120	5.1	53	
D2-120	6.3	29	32
D3-100	7.4	25	
D3-290	5.0	16	
D4-90	5.7	13	
H1-65	4.7	14	36
H2-110	6.0	14	38
H2-310	4.3	10	46
H3-70	7.7	17	
H4-80	5.8	24	
T5-110	7.6	19	
T6-120	15.2	13	
T2-210	8.0	10	38
T7-140	8.1	4	
T7-300	3.7	5	
R6-G	6.4	22	
R5-190	2.3	3	62
R4-G	4.1	3	
W2-G	2.4	5	52
W2-170	2.4	1	62
W2-250	1.3	1	64
S4-G	2.7	8	

contribution decreases with distance from the dunes. However, in section 4.4.5 the distribution of the sand and silt fraction along the length of the vlei is investigated and reveals that such a gradient of sand content as a result of proximity to the dunes does not appear to exist.

A more likely contributing factor is that more dissolved $CaCO_3$ is removed from the water column and transferred to the sediments in this area. This could occur here as a result of water remaining in this part of the vlei in dry periods. Calcium carbonate does not form part of the clay fraction of the sediments of De Hoop Vlei and, therefore, dilutes the amount of clay in the samples.

Another possible contributing factor is the flocculation of clay particles in the northern end of the vlei. An accumulation of clay in the upper parts of estuaries has been frequently noted. This occurs at the change in salinity between inflowing waters laden with suspended sediment and the saline waters of the estuaries because increased salinity facilitates clay flocculation. Water samples collected for this study indicate little difference in salinity between the Sout River inflow and the northern parts of the vlei. However, a salinity difference may occur at times of high river volume during storms, when much sediment would be transported in the river and the river salinity is likely to be low. Significant clay flocculation in the northern parts of the vlei during such times could contribute to the increased clay in this part of De Hoop Vlei.

Based on visual and tactile inspection, some cores may be divided into distinct depth sections with differing particle size distributions. In all cases measured, the clay content is greater in the lower sections of the sediment cores than in the surface sections. Where cores were divided into more than two depth sections, some cases of clay increasing with depth from the surface and then decreasing again at a lower depth occurred such as at M1. The different particle size distribution at different depths in the sediments is probably the result of varying depositional environments caused by variation in the volume of water inputs to the vlei.

The difference in particle size distribution between H1 and H2 is slight, suggesting that the sorting effects of wave action are not significant between these two points. The expected pattern is one of decreasing sediment grain sizes from the shore towards the centre of the basin (Forstner and Wittman, 1979). The absence of such a pattern here may be due to the very flat gradient of the vlei bottom. Such an effect may be significant for sediments closer to the edge of the vlei which are slightly elevated in relation to the vlei bottom and which would be affected by wave action during higher water levels.

The clay content is an important controlling factor on the chemical composition of the sediments with many trace elements being predominantly present in the clay fractions. This is discussed in more detail in section 4.4.5. Other aspects of silt and sand distribution are also discussed in section 4.4.5 in connection with SiO_2 concentrations.

4.4.2 Organic carbon

The method used to determine the organic C in the sediments can result in overestimates in reduced environments. This is because some dichromate, used to oxidise the organic matter, can also oxidise ferrous iron which is present in minerals. Because of the reduced nature of the De Hoop sediments and the fact that iron content differs between samples, there may, therefore, be some error in the determined values for organic C.

Organic C percentage of the sediment samples in the southern and central parts of the vlei generally varies between 1.7 and 8.7 percent but with two samples around 15 percent. At T6 there was evidence of vegetation throughout the sediment core which may account for the high value obtained. Organic C content in the Windhoek area is generally lower than further south with a variation between 1.3 and 2.7 percent. Based on the visual evidence of sediment colour, these samples were less reduced than other samples and conditions would therefore be less favourable for the accumulation of organic matter.

No other pattern of horizontal distribution of organic matter is evident from the data. An increase in organic matter with distance from the shoreline has, however, been noted in De Hoop Vlei by previous studies (Dunbar, 1996) and in other saline lake systems (Hammer, 1986). This has been explained by an increase in water depth from the shoreline and, therefore, a greater potential for organic matter production and subsequent sedimentation and accumulation of organic detritus.

A decrease in organic C with depth in the sediment samples was noted in all but one of the six cases where it was determined in both surface and sub-surface sections of a core. This is in keeping with the darker colour observed in the surface sections and can be explained by the sedimentation of organic detritus from the water column to the sediment surface.

4.4.3 Calcium carbonate

Calcium carbonate commonly constitutes more than 30 percent of the sediments by weight in moderately hard water lakes (Wetzel, 1983). The calcium carbonate concentrations of

sediment samples from De Hoop range between 1 and 63 percent with significantly higher values in the De Mond area and a general decrease northwards along the length of the vlei. The average value for surface sediments in the De Mond area is 54 percent. Slightly further north at D2 the carbonate concentration is only 29 percent, decreasing to around 15 percent in the De Hoop homestead region. The variation in $CaCO_3$ content along the length of the vlei is illustrated in Figure 4.1.

The higher concentrations of $CaCO_3$ at De Mond can be explained by the fact that much $CaCO_3$ is transferred from the water column to the sediments in this area when water remains here during dry periods. Evidence of the depletion of dissolved Ca in the water in this area has been discussed in section 3.4.3.1. Another influencing factor may be the contribution of calcareous wind-blown sands to the sediments in this area.

In the Tierhoek area, samples to the south of the spring have higher $CaCO_3$ contents than those to the north. The Tierhoek waters are all supersaturated with respect to calcite (see section 3.4.7) and, therefore, precipitation from these waters would be expected. The water at T7 is depleted in Ca compared to other Tierhoek waters (see section 3.4.3.1). However, from the lower $CaCO_3$ content in the sediments at this site it does not seem that more $CaCO_3$ is being precipitated here than at other sites in the Tierhoek area south of the spring.

The lowest $CaCO_3$ values occur in samples from W2. Water would not remain in this area during dry periods and the potential for precipitation is therefore limited in comparison to other sites. The higher value at S4 could be explained by the position of this site. The sample was taken in a water depth of 1.6 m, upstream of a causeway which dams the river. The water here was also supersaturated with respect to calcite. There is therefore potential for precipitation as water would remain here and be concentrated by evaporation during dry periods.

Decreases in $CaCO_3$ content with depth are evident at sites south of Tierhoek. These are all areas where transfer from the water column is likely to contribute significantly to the $CaCO_3$ content of surface sediments. At T7 this trend does not occur.

It is evident from mineralogical analysis of different size fractions (see section 4.4.7) that calcium carbonate does not form part of the clay fraction of the sediments. There is therefore a negative correlation between the $CaCO_3$ and clay contents. The correlation between the calcium carbonate concentration and other chemical parameters as well as the relationship to Ca and Mg concentrations is discussed in section 4.4.5.

4.4.4 Redox status

There is evidence of reducing conditions in much of the sedimentary environment of De Hoop Vlei. The most conclusive evidence obtained during the study was the change in colour of the sediments on exposure to air. Examination of the frozen cores, exposed to the atmosphere while thawing, showed that the surface changed from a very dark colour to a light brown over a period of several hours. The colour change took place to a depth of approximately 3 mm while the inside of the cores remained the same dark colour. Sediments stored in plastic jars showed this phenomenon well with the surface changing colour and the sediment below the surface remaining dark. On mixing of the sediment and covering of previously exposed brown areas so that they were no longer at the surface, they changed back to the dark colour over a few days.

This behaviour can be explained by the presence of sulphide minerals in the sediments which become oxidised on exposure to the atmosphere. Fanning *et al.* (1993) state that iron monosulphide minerals are recognised by the black colour that they impart to soil material and by the evolution of H_2S, with its characteristic rotten egg smell, when exposed to dilute HCl. Pyrite does not evolve H_2S in this manner. The De Hoop sediment samples did evolve H_2S when treated with dilute HCl in the laboratory, which confirmed the presence of iron monosulphides in the samples.

The literature on iron monosulphides in soils (which includes saturated wetland soils) has been reviewed by Fanning *et al.* (1993). These minerals are less prevalent than pyrite and do not occur in most sulphidic materials. They are extremely strong pigments and can cause a black colour even when present in small quantities. They are also extremely unstable and undergo colour changes, with fading of the black colour, upon exposure to air. Studies have shown that monosulphides form rapidly when Fe oxide bearing soil materials are buried in tidal marshes. They appear to form only when there is an abundance of Fe or in rapidly accumulating marsh sediments. Tidal marsh soils that are subject to slow rates of sedimentation of mineral soil materials, and thus slow rates of Fe addition, have not been found to contain monosulphides. The presence of these minerals is evidence of reducing conditions in the sediments. Further evidence of reducing conditions was the smell of H_2S gas in the field.

Some sediments examined in the field and some of the frozen cores had a thin layer (less than 1 cm) of a light brown colour at the surface which was underlain by darker (black) material. This would be brought about by oxygen diffusion from the water column into the sediments.

The oxygen demand of the sediments would prevent O_2 diffusion beyond a certain depth.

Samples collected from the Rietkloof and Windhoek areas in the north of the vlei showed different behaviour with respect to colour changes. The sediments from the Rietkloof area were all taken where no surface water was present. At R6 and R5 the sediments were, however, still moist. These showed only some evidence of darker material 1 cm below the surface with the majority of the core a light and much richer brown in colour compared to other sediments. The core from W2 had no dark coloration and was uniformly brown throughout its length. After air drying these sediments were a richer brown in comparison to the gleyed colour of the other air-dried sediments.

The absence of reducing conditions in these sediments in the north of the vlei can be explained by the lack of continual water cover and the drying and oxidation of the sediments during dry periods. The flow of oxygen to some depth can take place more easily through dry pore spaces.

Oxidation of reduced sediments can cause oxidation of sulphide minerals and consequent production of sulphuric acid which results in a lowering of the pH of the sediments. Such changes could have important ecological implications. In order to measure the changes in pH following drying of the De Hoop sediments, pH was measured in two wet sediment samples before exposure to the atmosphere and in the same sediments after air drying. The results of these determinations are given in Table 4.2.

Table 4.2 Results of the pH measurements on oxidised (dried) and reduced (wet) sediments. The repeat measurement was done after the samples were sealed from contact with the atmosphere for 8 weeks.

Sample	Repetition	Redox state	
		Wet	Dry
M1-G	1	8.11	8.68
	2	7.41	8.07
S4-G	1	8.05	8.33
	2	7.83	7.48

The results are somewhat surprising in that, when the first measurements were done, the pH of dried sediments was higher than that of the non-dried ones. After equilibrating for 8 weeks the pH of the dried sediment at M1 was still higher than that of the wet sample but the pH of the dried S4 sample was 0.35 pH units lower than that of the wet one. Sample M1 was highly buffered against acidification due to the high carbonate content. Sample S4 was much less buffered which could explain why it showed different behaviour.

At the time of the initial pH measurement the dried sample suspensions were brown in colour while the wet ones were black. After 8 weeks the dried sediment suspensions had changed colour from brown to black, indicating the onset of reducing conditions. Between first and second readings the pH dropped in all cases. This lowering of pH between measurements and the lower pH in interstitial waters (see section 3.4.2) suggests that anaerobic conditions are resulting in a lowering of pH. This can possibly be explained by a slow rate of gas exchange between sediments and water under anaerobic conditions. This would lead to an increase in the production of CO_2 and of protonated species following anaerobic oxidation of organic matter and therefore cause a lowering of pH (Ben-Yaakov, 1973; Mackenzie *et al.*, 1995). The higher pH after drying of the samples may, therefore, be explained by oxidising conditions, which prevent the acidifying effects of reducing conditions from playing a role.

The conclusion from this is that acidification resulting from the oxidation of sulphide minerals is unimportant in the De Hoop Vlei environment, and is overridden by the lowering of pH under reducing conditions. The negligible effect of sulphide oxidation can be explained by a low concentration of such minerals and the high buffering effect of carbonates in the sediments.

4.4.5 Elemental composition of the sediments

The results of major element analyses on sediment samples are given in Table 4.3. The results of trace element analyses are given in Table 4.4. Data from the sediment samples collected from the Rietkloof area proved to be unreliable in that summation of the major elements resulted in totals of greater than 110 percent. These data are, therefore, not included in Tables 4.3 and 4.4. According to J.P. Willis (pers. com.) the explanation for this lies in the fact that these samples were taken where no surface water was present. High concentrations of Na salts in the interstitial waters following evaporative concentration would result in the formation of salt crystals in the samples during drying (in the laboratory for samples R5 and R6 and in the field for R4). In the briquettes prepared for XRFS analysis these salts are able to dissolve in any moisture present. Under vacuum when moisture is drawn from the briquettes, these salts

Table 4.3 Results of the XRF major element analyses on sediment samples from De Hoop Vlei. Values are given in mass percent of the relevant oxides. H_2O values which were determined separately are included. The total is the sum of all values including CO_2 and organic matter

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	S	H_2O	TOT
M1-90	29.16	0.19	3.23	1.06	1.41	27.47	0.73	0.62	0.16	0.55	0.43	1.35	95.5
M1-255	39.16	0.52	11.07	3.25	1.29	15.84	0.68	2.29	0.15	0.33	0.37	5.07	99.6
M1-290	33.01	0.36	8.02	2.01	1.16	22.74	0.56	1.60	0.17	0.26	0.18	4.02	98.1
M2-160	31.07	0.23	2.97	1.03	1.16	27.62	0.74	0.59	0.15	0.54	0.45	2.22	93.5
M3-100	28.03	0.22	3.93	1.16	1.74	26.87	0.70	0.70	0.17	0.36	0.48	2.84	96.6
M4-135	19.29	0.17	4.52	1.19	1.87	27.46	1.35	0.84	0.18	1.03	0.62	5.38	96.2
M5-150	12.52	0.18	4.37	1.84	1.89	20.66	1.13	0.89	0.19	1.07	0.98	5.87	95.1
M6-70	22.09	0.13	1.80	1.01	1.62	29.80	0.86	0.37	0.25	0.75	0.47	4.49	94.7
M7-160	22.66	0.31	8.30	2.52	2.28	19.81	1.21	1.54	0.21	1.15	1.03	4.03	98.7
M8-160	20.68	0.15	2.58	0.94	1.42	31.50	0.64	0.50	0.21	0.48	0.47	3.74	93.8
M9-120	17.25	0.23	5.77	1.88	2.09	23.60	0.77	1.15	0.19	0.62	0.83	3.95	93.6
M9-240	31.68	0.49	12.28	3.48	1.96	15.70	0.80	2.32	0.18	0.52	0.98	5.43	101.4
M10-12	22.46	0.26	7.21	1.97	2.25	23.46	0.87	1.28	0.18	0.75	0.95	4.97	98.2
D2-120	38.00	0.59	14.21	4.66	2.28	11.09	0.89	2.74	0.14	0.64	1.74	3.10	103.1
D3-100	36.39	0.59	14.30	4.81	2.76	9.77	0.86	2.75	0.16	0.77	1.68	4.83	102.4
D3-290	48.33	0.73	15.61	5.05	1.70	6.61	0.85	3.15	0.11	0.50	0.96	5.09	103.7
D4-90	46.56	0.74	16.74	6.30	1.80	5.36	0.69	3.29	0.12	0.32	1.29	6.80	105.0
H1-65	39.56	0.73	15.52	7.23	2.08	6.03	0.55	3.31	0.13	0.33	0.56	9.52	99.4
H2-110	38.34	0.67	14.39	6.60	1.65	6.44	0.84	3.04	0.12	0.69	0.73	11.11	100.2
H2-310	50.38	0.76	16.06	6.20	1.52	4.84	0.74	3.25	0.10	0.32	0.26	7.66	103.5
H3-70	31.01	0.58	11.93	6.65	1.54	8.28	0.83	2.73	0.12	0.98	0.93	8.56	93.9
H4-80	30.85	0.55	12.11	5.96	2.21	10.98	0.48	2.61	0.15	0.30	0.87	8.71	95.7
T5-110	35.95	0.64	12.88	6.52	1.20	8.77	0.24	2.80	0.12	0.05	1.82	3.54	94.8
T6-120	34.22	0.58	11.69	4.83	0.89	7.49	0.28	2.29	0.12	0.07	1.78	5.30	99.4
T2-210	40.82	0.71	14.77	7.22	1.07	4.78	0.25	3.09	0.14	0.04	0.78	8.50	99.3
T7-140	37.94	0.70	14.21	10.49	1.26	1.96	0.41	3.14	0.19	0.25	0.86	10.64	96.7
T7-300	50.62	0.83	18.58	9.81	1.43	2.37	0.46	3.54	0.16	0.14	0.21	9.28	105.7
W2-G	42.72	0.83	14.97	7.25	1.95	2.86	9.17	3.26	0.14	4.23	0.17	9.91	103.7
W2-170	49.50	1.00	18.53	7.99	1.15	0.32	0.61	4.14	0.11	0.44	0.08	8.85	97.0
W2-250	50.24	0.94	17.30	7.78	1.13	0.24	0.63	3.87	0.09	0.45	0.09	8.98	94.1
S4-G	39.65	0.77	14.92	6.69	2.39	3.14	0.71	3.46	0.17	0.77	0.78	12.94	94.1

Table 4.4 The results of all trace element analyses (mg/kg) by XRFS on sediment samples from De Hoop Vlei. Blank values are below detection limits.

Sample	Sr	Ba	Mn	Zr	Rb	V	Cr	Zn	Cu	Ni	Y	Pb	Sc	Co	Nb	Th	U	Mo
M1-90	1587	133	185	254	25	18	26	13	7.3	8.7	11	8.1	2.6	3.0	5.0	4.6	3.5	
M1-255	894	391	210	205	101	80	73	56	19	25	23	16	16	9.5	11	9.7	4.5	
M1-290	1269	284	218	224	67	49	48	38	14	16	17	13	11	6.0	8.0	8.1	3.6	
M2-160	1496	115	130	514	22	18	31	12	7.4	8.2	11	6.2	4.3	3.2	6.6	3.7	3.3	
M3-100	1673	140	143	358	29	22	31	16	8.2	10	9.1	8.2	2.6	3.6	5.3	4.1	6.8	1.1
M4-135	1708	169	173	119	30	24	28	18	9.0	10	8.3	7.8	2.8	3.8	3.6	4.7	5.8	
M5-150	1324	191	191	87	43	31	30	28	44	14	7.1	13	5.2	5.3	3.9	5.1	19	1.1
M6-70	1869	111	204	303	15	10	22	14	7.6	7.1	6.3	15		2.2	3.7	4.7	9.5	
M7-160	1225	296	308	128	66	50	47	37	14	20	13	16	10	6.9	6.1	6.6	8.7	1.0
M8-160	1840	113	190	223	19	15	22	11	7.3	7.1	7.4	13		1.9	3.7	5.3	4.7	
M9-120	1401	246	254	140	52	39	37	28	27	16	9.3	11	6.6	5.1	4.9	5.6	15	1.5
M9-240	1031	429	311	139	98	81	69	56	19	26	16	15	16	12	9.8	7.4	10	
M10-120	1477	251	228	151	50	42	39	27	12	16	10	11	7.3	7.2	6.1	3.9	12	1.1
D2-120	727	506	468	139	122	99	82	62	18	30	23	22	18	12	11	11	12	1.7
D3-100	617	541	423	122	128	103	83	62	19	32	22	24	18	13	12	10	14	2.0
D3-290	347	576	279	159	146	119	97	82	24	35	31	24	20	16	14	12	4.2	
D4-90	332	648	410	126	162	130	103	75	22	38	29	25	21	17	15	13	7.3	1.1
H1-65	362	617	459	118	167	126	98	74	55	36	28	26	20	18	14	12	8.4	
H2-110	382	572	383	117	152	115	89	70	33	35	26	27	19	16	13	12	7.8	0.9
H2-310	277	609	242	172	154	127	101	82	24	37	32	25	21	16	15	14	4.1	0.8
H3-70	447	480	423	104	138	95	76	64	41	33	23	27	17	14	12	12	9.0	1.6
H4-80	580	486	669	93	132	91	75	61	25	30	21	26	17	12	11	10	10.5	
T5-110	424	497	421	116	137	101	81	70	34	33	27	25	18	14	13	11	4.7	
T6-120	276	415	203	145	122	89	78	63	26	32	28	28	16	12	12	13	6.7	1.0
T2-210	207	572	474	115	149	121	95	73	22	35	26	26	20	18	13	13	6.6	1.2
T7-140	164	571	386	113	166	123	95	83	34	40	27	26	18	23	14	12	8.0	
T7-300	179	741	404	129	180	149	119	83	24	42	32	28	23	23	17	15	3.5	1.6
W2-G	282	626	1628	143	165	137	108	71	28	37	36	26	21	21	16	15	3.9	
W2-170	119	697	418	161	214	163	118	79	30	42	40	31	24	19	20	17	4.1	
W2-250	94	671	286	154	203	140	113	83	29	44	39	33	21	19	19	17	5.0	1.1
S4-G	357	561	334	138	170	119	93	76	27	37	32	23	19	15	16	13	6.6	

are precipitated on the surface of the briquettes. This results in an overestimation of Na and Cl during XRFS analysis and consequent errors in other elements. Comparatively high concentrations of Na and Cl were obtained for the three samples from the Rietkloof area. The precipitation of NaCl on the surface of briquettes could have been prevented by dialysis of the sediment samples prior to making the briquettes.

In order to investigate the relationships between different elements a Pearsons product moment correlation matrix was performed with all the measured variables using STATISTICA software. The results of this are given in Table 4.5. A principal component analysis (PCA) was also performed, using the same software. The results of this are given in Appendix 5. Prior to these statistical analyses, the data were investigated for outlier values (defined as being > mean + 1.96 std deviations or < mean - 1.96 std deviations). The correlation matrix was performed with all outlier values excluded. The PCA was performed without sample W2-G, which had outlier values for Na, Cl and Mn. Molybdenum concentrations were close to detection limits and the accuracy of these values is therefore questionable. For this reason correlations involving Mo are omitted from the discussion.

The sediments of De Hoop Vlei may be regarded as consisting of four major components, namely resistate minerals, carbonate minerals, clay minerals and organic matter. Elements are distributed differently among these four fractions. By examining various correlations it is possible to make conclusions about the distribution of different elements among the four fractions and to determine which variables represent each fraction most effectively.

Aluminium is likely to occur predominantly as a component of clay minerals. It has a strong positive correlation with clay percentage, although correlations between clay percent and many trace metals (eg Y, Nb, Th) as well as the major oxides TiO_2, Fe_2O_3 and K_2O are higher. In the absence of clay percentage data for many samples, the concentration of Al_2O_3 may be used as a good indication of this parameter.

Using Al_2O_3 concentrations as an indication of clay percentage, the clay distribution in the vlei can be further examined. The patterns of variation in Al_2O_3 concentration confirm that clay percentages increase with depth in all the cases where measurements at different depths were done and that they increase northwards along the vlei. Sorting effects due to wave action are not evident.

Silica is usually a good indication of the sand fraction of sediments. However SiO_2 occurs in both quartz and in clay minerals. In many of the De Hoop samples, the carbonate

Table 4.5 Pearsons product moment correlation matrix for all measured variables of sediment samples from De Hoop Vlei. Correlations were performed using STATISTICA software. (n = 14 for correlations involving clay %; n = 28 for those involving Sc; n = 30 for all other correlations)

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	S	H_2O	CO_2	OM	Clay%
SiO_2	1.00	0.92	0.89	0.77	-0.32	-0.85	-0.40	0.88	-0.75	-0.49	-0.13	0.51	-0.86	-0.10	0.88
TiO_2	0.92	1.00	0.97	0.90	-0.24	-0.97	-0.42	0.99	-0.75	-0.39	0.00	0.69	-0.97	0.07	0.97
Al_2O_3	0.89	0.97	1.00	0.89	-0.10	-0.97	-0.34	0.99	-0.72	-0.34	0.11	0.65	-0.94	0.15	0.90
Fe_2O_3	0.77	0.90	0.89	1.00	-0.26	-0.94	-0.50	0.91	-0.56	-0.40	0.04	0.78	-0.95	0.19	0.92
MgO	-0.32	-0.24	-0.10	-0.26	1.00	0.19	0.60	-0.15	0.33	0.63	0.35	-0.07	0.28	0.00	-0.47
CaO	-0.85	-0.97	-0.97	-0.94	0.19	1.00	0.43	-0.98	0.71	0.36	-0.14	-0.73	0.99	-0.25	-0.93
Na_2O	-0.40	-0.42	-0.34	-0.50	0.60	0.43	1.00	-0.37	0.33	0.90	-0.07	-0.23	0.48	-0.22	-0.23
K_2O	0.88	0.99	0.99	0.91	-0.15	-0.98	-0.37	1.00	-0.73	-0.33	0.07	0.71	-0.97	0.11	0.94
P_2O_5	-0.75	-0.75	-0.72	-0.56	0.33	0.71	0.33	-0.73	1.00	0.38	-0.09	-0.31	0.71	-0.11	-0.89
Cl	-0.49	-0.39	-0.34	-0.40	0.63	0.36	0.90	-0.33	0.38	1.00	0.02	-0.08	0.40	-0.11	-0.12
S	-0.13	0.00	0.11	0.04	0.35	-0.14	-0.07	0.07	-0.09	0.02	1.00	-0.22	-0.09	0.75	-0.37
H_2O	0.51	0.69	0.65	0.78	-0.07	-0.73	-0.23	0.71	-0.31	-0.08	-0.22	1.00	-0.74	-0.01	0.78
CO_2	-0.86	-0.97	-0.94	-0.95	0.28	0.99	0.48	-0.97	0.71	0.40	-0.09	-0.74	1.00	-0.24	-0.93
OM	-0.10	0.07	0.15	0.19	0.00	-0.25	-0.22	0.11	-0.11	-0.11	0.75	-0.01	-0.24	1.00	-0.27
Clay%	0.88	0.97	0.90	0.92	-0.47	-0.93	-0.23	0.94	-0.89	-0.12	-0.37	0.78	-0.93	-0.27	1.00
Sr	-0.85	-0.96	-0.95	-0.93	0.25	0.99	0.49	-0.96	0.75	0.42	-0.17	-0.69	0.99	-0.31	-0.91
Ba	0.89	0.97	0.99	0.92	-0.12	-0.97	-0.37	0.99	-0.70	-0.35	0.08	0.69	-0.95	0.14	0.91
Mn	0.36	0.55	0.61	0.65	0.21	-0.61	-0.31	0.62	-0.33	-0.17	0.33	0.47	-0.58	0.25	0.48
Zr	-0.25	-0.51	-0.61	-0.59	-0.18	0.61	0.06	-0.60	0.36	-0.05	-0.42	-0.50	0.57	-0.49	-0.48
Rb	0.87	0.99	0.97	0.93	-0.20	-0.99	-0.41	0.99	-0.72	-0.35	0.04	0.74	-0.98	0.13	0.96
V	0.90	0.99	0.99	0.93	-0.18	-0.98	-0.40	0.99	-0.71	-0.37	0.06	0.70	-0.97	0.13	0.93
Cr	0.92	0.99	0.99	0.92	-0.20	-0.98	-0.41	0.99	-0.72	-0.40	0.05	0.68	-0.97	0.13	0.93
Zn	0.87	0.96	0.97	0.92	-0.18	-0.98	-0.42	0.98	-0.70	-0.39	0.14	0.68	-0.97	0.22	0.88
Cu	0.50	0.73	0.71	0.80	-0.21	-0.80	-0.40	0.77	-0.58	-0.20	0.20	0.66	-0.80	0.37	0.72
Ni	0.86	0.98	0.98	0.94	-0.17	-1.00	-0.41	0.99	-0.71	-0.36	0.13	0.71	-0.98	0.22	0.93
Y	0.93	0.99	0.94	0.87	-0.32	-0.95	-0.44	0.96	-0.78	-0.42	-0.02	0.65	-0.96	0.07	0.98
Pb	0.77	0.91	0.87	0.89	-0.27	-0.93	-0.47	0.90	-0.67	-0.35	0.15	0.67	-0.94	0.28	0.94
Sc	0.85	0.95	0.99	0.86	-0.21	-0.95	-0.42	0.98	-0.61	-0.37	0.06	0.62	-0.93	0.07	0.85
Co	0.84	0.93	0.94	0.97	-0.23	-0.96	-0.43	0.94	-0.61	-0.39	0.04	0.74	-0.95	0.18	0.90
Nb	0.92	1.00	0.96	0.89	-0.27	-0.97	-0.43	0.98	-0.75	-0.39	-0.03	0.69	-0.97	0.05	0.98
Th	0.89	0.97	0.92	0.87	-0.34	-0.95	-0.43	0.95	-0.75	-0.39	-0.02	0.68	-0.96	0.12	0.97
U	-0.45	-0.26	-0.14	-0.17	0.71	0.15	0.28	-0.17	0.34	0.42	0.52	-0.10	0.22	0.39	-0.32

Table 4.5 continued

	Sr	Ba	Mn	Zr	Rb	V	Cr	Zn	Cu	Ni	Y	Pb	Sc	Co	Nb	Th	U
SiO_2	-0.85	0.89	0.36	-0.25	0.87	0.90	0.92	0.87	0.50	0.86	0.93	0.77	0.85	0.84	0.92	0.89	-0.45
TiO_2	-0.96	0.97	0.55	-0.51	0.99	0.99	0.99	0.96	0.73	0.98	0.99	0.91	0.95	0.93	1.00	0.97	-0.26
Al_2O_3	-0.95	0.99	0.61	-0.61	0.97	0.99	0.99	0.97	0.71	0.98	0.94	0.87	0.99	0.94	0.96	0.92	-0.14
Fe_2O_3	-0.93	0.92	0.65	-0.59	0.93	0.93	0.92	0.92	0.80	0.94	0.87	0.89	0.86	0.97	0.89	0.87	-0.17
MgO	0.25	-0.12	0.21	-0.18	-0.20	-0.18	-0.20	-0.18	-0.21	-0.17	-0.32	-0.27	-0.21	-0.23	-0.27	-0.34	0.71
CaO	0.99	-0.97	-0.61	0.61	-0.99	-0.98	-0.98	-0.98	-0.80	-1.00	-0.95	-0.93	-0.95	-0.96	-0.97	-0.95	0.15
Na_2O	0.49	-0.37	-0.31	0.06	-0.41	-0.40	-0.41	-0.42	-0.40	-0.41	-0.44	-0.47	-0.42	-0.43	-0.43	-0.43	0.28
K_2O	-0.96	0.99	0.62	-0.60	0.99	0.99	0.99	0.98	0.77	0.99	0.96	0.90	0.98	0.94	0.98	0.95	-0.17
P_2O_5	0.75	-0.70	-0.33	0.36	-0.72	-0.71	-0.72	-0.70	-0.58	-0.71	-0.78	-0.67	-0.61	-0.61	-0.75	-0.75	0.34
Cl	0.42	-0.35	-0.17	-0.05	-0.35	-0.37	-0.40	-0.39	-0.20	-0.36	-0.42	-0.35	-0.37	-0.39	-0.39	-0.39	0.42
S	-0.17	0.08	0.33	-0.42	0.04	0.06	0.05	0.14	0.20	0.13	-0.02	0.15	0.06	0.04	-0.03	-0.02	0.52
H_2O	-0.69	0.69	0.47	-0.50	0.74	0.70	0.68	0.68	0.66	0.71	0.65	0.67	0.62	0.74	0.69	0.68	-0.10
CO_2	0.99	-0.95	-0.58	0.57	-0.98	-0.97	-0.97	-0.97	-0.80	-0.98	-0.96	-0.94	-0.93	-0.95	-0.97	-0.96	0.22
OM	-0.31	0.14	0.25	-0.49	0.13	0.13	0.13	0.22	0.37	0.22	0.07	0.28	0.07	0.18	0.05	0.12	0.39
Clay%	-0.91	0.91	0.48	-0.48	0.96	0.93	0.93	0.88	0.72	0.93	0.98	0.94	0.85	0.90	0.98	0.97	-0.32
Sr	1.00	-0.96	-0.61	0.62	-0.97	-0.97	-0.97	-0.98	-0.82	-0.99	-0.95	-0.93	-0.95	-0.94	-0.95	-0.95	0.18
Ba	-0.96	1.00	0.64	-0.61	0.98	0.99	0.99	0.97	0.74	0.98	0.94	0.90	0.98	0.96	0.96	0.93	-0.14
Mn	-0.61	0.64	1.00	-0.66	0.62	0.61	0.58	0.60	0.57	0.61	0.46	0.64	0.60	0.60	0.52	0.50	0.29
Zr	0.62	-0.61	-0.66	1.00	-0.58	-0.58	-0.55	-0.61	-0.65	-0.62	-0.45	-0.56	-0.51	-0.59	-0.47	-0.48	-0.25
Rb	-0.97	0.98	0.62	-0.58	1.00	0.99	0.98	0.97	0.79	0.99	0.97	0.93	0.96	0.95	0.99	0.96	-0.19
V	-0.97	0.99	0.61	-0.58	0.99	1.00	1.00	0.98	0.75	0.99	0.96	0.91	0.98	0.96	0.98	0.95	-0.19
Cr	-0.97	0.99	0.58	-0.55	0.98	1.00	1.00	0.98	0.72	0.99	0.97	0.90	0.98	0.96	0.98	0.95	-0.21
Zn	-0.98	0.97	0.60	-0.61	0.97	0.98	0.98	1.00	0.79	0.99	0.94	0.90	0.97	0.95	0.95	0.93	-0.17
Cu	-0.82	0.74	0.57	-0.65	0.79	0.75	0.72	0.79	1.00	0.80	0.71	0.79	0.67	0.76	0.73	0.73	0.03
Ni	-0.99	0.98	0.61	-0.62	0.99	0.99	0.99	0.99	0.80	1.00	0.95	0.93	0.96	0.96	0.97	0.95	-0.13
Y	-0.95	0.94	0.46	-0.45	0.97	0.96	0.97	0.94	0.71	0.95	1.00	0.90	0.92	0.89	0.99	0.98	-0.36
Pb	-0.93	0.90	0.64	-0.56	0.93	0.91	0.90	0.90	0.79	0.93	0.90	1.00	0.91	0.88	0.90	0.94	-0.13
Sc	-0.95	0.98	0.60	-0.51	0.96	0.98	0.98	0.97	0.67	0.96	0.92	0.91	1.00	0.91	0.94	0.92	-0.17
Co	-0.94	0.96	0.60	-0.59	0.95	0.96	0.96	0.95	0.76	0.96	0.89	0.88	0.91	1.00	0.92	0.88	-0.17
Nb	-0.95	0.96	0.52	-0.47	0.99	0.98	0.98	0.95	0.73	0.97	0.99	0.90	0.94	0.92	1.00	0.97	-0.29
Th	-0.95	0.93	0.50	-0.48	0.96	0.95	0.95	0.93	0.73	0.95	0.98	0.94	0.92	0.88	0.97	1.00	-0.30
U	0.18	-0.14	0.29	-0.25	-0.19	-0.19	-0.21	-0.17	0.03	-0.13	-0.36	-0.13	-0.17	-0.17	-0.29	-0.30	1.00

concentration is high. As a result SiO_2 correlates positively with clay percentage and many of the elements associated with clays. This is because when carbonates are high both the clay and sand fractions are lower as a result, and when carbonates are lower both of these are high (see Fig. 4.1).

Another resistate mineral, which usually occurs predominantly in the sand and silt fractions, is zircon. The concentrations of Zr give a good indication of the concentrations of this mineral. There is no correlation between Zr and SiO_2 in the De Hoop data. In a similar study on the sediments of Barber's Pan this correlation was found to be strongly positive (Knesl, 1996). Zirconium has a strongly negative correlation with all variables associated with the clay fraction, which is to be expected. However, it shows a positive correlation with CaO, CO_2, and Sr which is unusual. The reason for this is unknown.

The CaO to CO_2 ratio gives an indication of the quantity of carbonate minerals which are $CaCO_3$. By a calculation of the equivalent mass of CO_2 and CaO in comparison to $CaCO_3$ it can be seen that the ratio of CaO to CO_2 should be 1.27 if all Ca is in the form of $CaCO_3$. A higher ratio means that there is excess Ca which is present in another form. A lower ratio means that other carbonate minerals exist in addition to $CaCO_3$. The CaO to CO_2 ratio for all the samples is given in Table 4.6. These ratios are all below 1.27 except for sample T6-120. This indicates the presence of other carbonate minerals which are likely to be Mg carbonates. The excess CO_2 not accounted for in $CaCO_3$ was calculated and the ratio of MgO to this excess CO_2 is also given in Table 4.6. By a calculation of the equivalent mass of CO_2 and MgO in comparison to $MgCO_3$ it can be seen that the ratio of MgO to CO_2 should be 0.92 if all Mg is in the form of $MgCO_3$. A higher ratio means that there is excess Mg which is present in another form. A lower ratio means that other carbonate minerals exist in addition to $MgCO_3$. In evaluating these ratios it should be remembered that CaO and MgO were determined with ±10 percent error and some variation in the ratios may be the result of this error.

The results in Table 4.6 show that in the southern parts of the vlei all Mg is accounted for in carbonates with some excess carbonate minerals indicated by the low ratios. In the northern parts of the vlei, on the other hand, there is excess Mg. Magnesium is, therefore, probably present in the form of carbonate minerals in the southern parts and associated with clays in the northern parts where, the clay content of the sediments is high. This would explain the correlation results for MgO, particularly the lack of correlation with either carbonates or clay content.

Table 4.6 The calculated CaO to CO_2 and MgO to excess CO_2 ratios for the sediment samples from De Hoop Vlei. The mass ratio for equivalent quantities is 1.27 and 0.92 for CaO and MgO, respectively.

Sample	CaO/CO_2	MgO/ excess CO_2
M1-90	1.13	0.51
M1-255	1.13	0.86
M1-290	1.10	0.43
M2-160	1.26	5.44
M3-100	1.07	0.45
M4-135	1.06	0.45
M5-150	1.01	0.44
M6-70	1.13	0.57
M7-160	1.00	0.55
M8-160	1.13	0.48
M9-120	0.99	0.39
M9-240	0.96	0.49
M10-120	1.00	0.45
D2-120	0.86	0.55
D3-100	0.89	0.85
D3-290	0.93	0.91
D4-90	0.91	1.06
H1-65	0.96	1.38
H2-110	1.07	1.71
H2-310	1.05	1.90
H3-70	1.13	1.90
H4-80	1.03	1.09
T5-110	1.07	0.91
T6-120	1.36	
T2-210	1.11	2.02
T7-140	1.16	8.83
T7-300	0.99	2.65
W2-G	1.19	12.25
W2-170	0.71	5.66
W2-250	0.86	12.46
S4-G	0.93	2.68

From the correlation results presented in Table 4.5, there is no correlation between MgO and CaO or CO_2. The only variables showing a significant correlation with Mg are U, Na and Cl which show positive correlations. The correlation between Mg and Na and Cl may be the result of precipitation of soluble Mg minerals during sample drying. There is no correlation between MgO and clay percentage or any variable associated with clay percentage. It is also

possible that some Mg exists as one of the silicate minerals identified as being supersaturated in the vlei water, according to the saturation indices calculated in section 3.4.7.

Potassium shows a strong positive correlation with clay percentage and all other variables associated with it. It is likely that it occurs almost exclusively in the sediments as adsorbed K^+ ions in the inter-layer spaces of micaceous clay minerals.

Sodium and chloride show a strong positive correlation with each other which suggests that Na occurs predominantly as halite in the sediments. Precipitation of halite would, however, only occur from interstitial waters during drying of the samples and would not be present under saturated conditions in the field. The samples from the Tierhoek area, where salinity of the waters is lower, show a lower Na and Cl concentration compared to samples from elsewhere in the study area. Sample W2-G is enriched in Na, Cl and Mn. This was the only sample taken of purely surface sediments to a depth of only a few millimetres which appeared to be recently deposited.

The changing proportions of the four different sediment components along the length of the vlei were investigated. For this purpose clay percent was estimated from Al_2O_3 values using the linear regression relationship between Al_2O_3 and clay percent ($r^2 = 0.77$; $n = 14$). The values for clay were summed with carbonate and organic matter values and the sum subtracted from 100 to give an estimate of the percentage of the non-calcareous sand and silt fraction. The variation of the four components along the length of the vlei is illustrated in Figure 4.1.

There is a positive correlation between clay percentage and the amount of H_2O in the briquettes. This is to be expected as clay minerals contain structural water and bind available moisture strongly.

From the results in Table 4.5 it appears that phosphorus is associated primarily with calcium in the De Hoop sediments and not with organic matter or clay minerals. Phosphate shows a number of significant correlations. Positive correlations exist with CaO, CO_2 and Sr. Negative correlations exist with all variables associated with clay minerals. No correlation exists with organic matter. The dominant form of phosphorus is therefore inorganic in the sediments and it probably occurs as an apatite mineral or as co-precipitated P with carbonate minerals.

The correlation results suggest that sulphur in the De Hoop sediments is associated predominantly with organic matter. The only other significant correlations are a weakly

positive one with U, which is also weakly correlated with organic matter, and a weakly negative one with Zr. The fact that there is no correlation between Fe and S suggests that iron sulphide minerals are present in only small quantities.

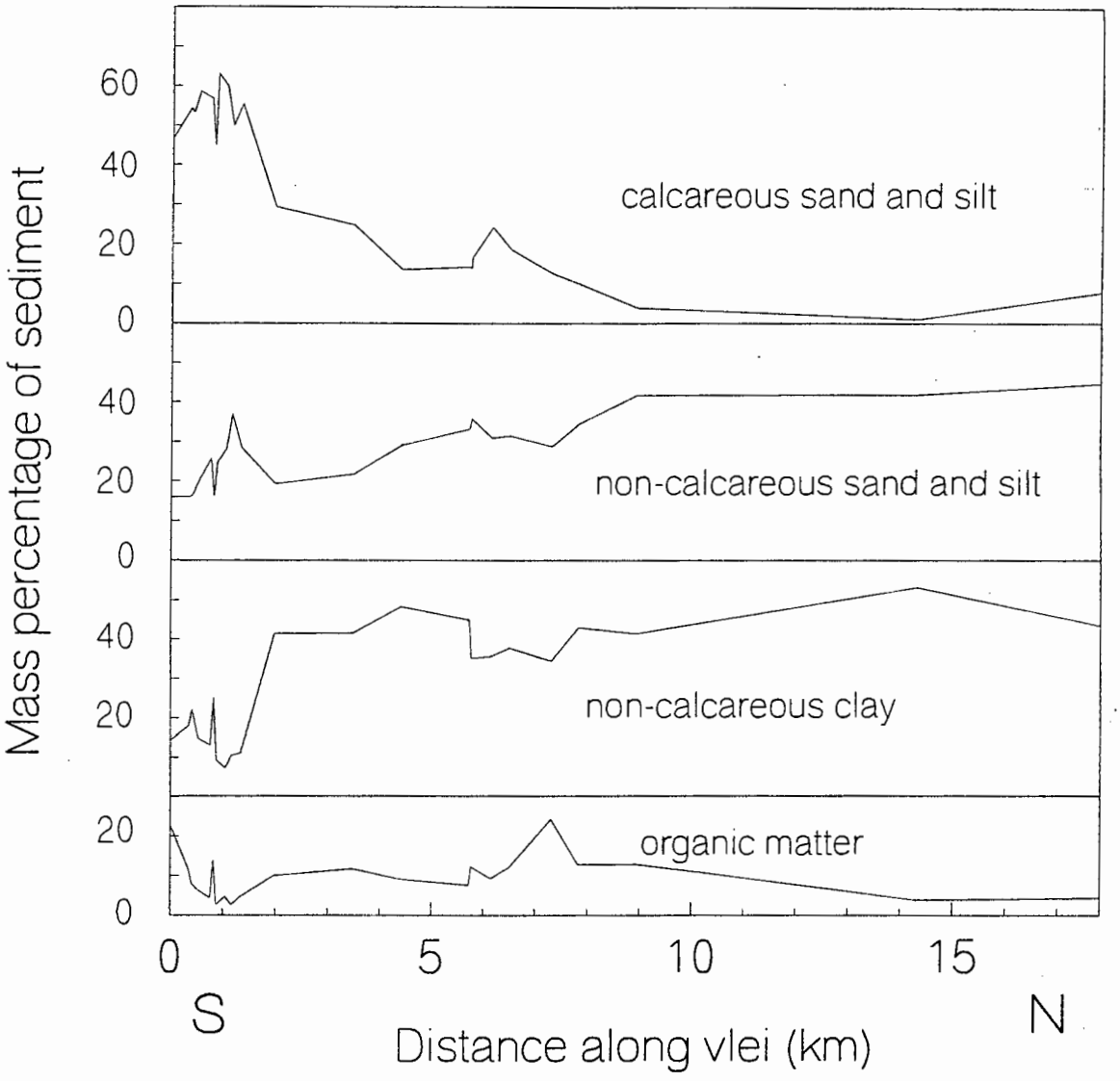

Figure 4.1 The variation of the four major sediment components in surface samples with distance from the southern end of the vlei. Approximate distances are relative to a line along the centre of the vlei starting at position M5. Calcareous sand and silt values are those determined for $CaCO_3$ and organic matter values are those determined by analysis. Non-calcareous clay was estimated from Al concentrations and non-calcareous sand and silt was estimated by subtracting the total of the other three components from 100 percent.

Correlations between trace elements and organic matter and clay percent suggest that most trace elements are associated with clay minerals rather than with organic matter. All trace

metals except Sr, Zr, Mn, Cu and U show strong positive correlations with clay percentage and other variables associated with it. Copper shows a positive correlation but it is slightly weaker, and Mn shows a still weaker correlation than that of the other trace metals. Mn shows the strongest positive correlation with Fe. However, the correlation between Mn and Fe is weaker than that between Fe and other trace metals associated with the clay fraction. A strong positive correlation exists between Ca and Sr. This is expected as Sr is readily able to substitute for Ca in $CaCO_3$ minerals (Wehmiller, 1972). Zirconium is expected to occur predominantly in the resistate mineral zircon.

Uranium is an exception to other trace metals. It has no correlation with clay percent but a very weak positive correlation with organic matter. The strongest correlation is a positive one with Mg. Uranium is also positively correlated with S and Cl and negatively correlated with SiO_2.

The co-precipitation of heavy metals with carbonate minerals can be an important mechanism for the removal of these metals from solution (Forstner and Wittman, 1979). This is only likely to occur, however, where trace metals are present in high enough concentrations to saturate other elemental sinks (Jenne, 1976, cited in Forstner and Wittman, 1979). Heavy metal concentrations in De Hoop Vlei are relatively low and therefore association between heavy metals and CaO would not be expected. The correlations of most trace metals with CaO is strongly negative which confirms this expectation. Exceptions are Mn which is more weakly negative, Zr which shows a weak positive correlation, U which shows no correlation and Sr which has been discussed above.

The principal components analysis of the data showed that 94 percent of the total variance was explained by the first five multi-variate factors, with 69 percent explained by the first one and 81 percent by the first two factors. The variable loadings on the factors indicate that the first factor reflects two components, a clay rich component represented by high positive loadings for Al_2O_3 and all other elements identified above as being associated with the clay fraction, and a carbonate component represented by high negative loadings for CaO, CO_2 and Sr. The highest positive loading for SiO_2 is also on factor one as well as the highest negative loading for P_2O_5. The second factor also reflects two components, an organic matter component represented by high loadings for organic matter as well as S and U and a second component represented by a negative loading for Zr. Factor three is an NaCl factor, factor four has moderate positive loadings for H_2O and Cu, and factor five has the highest loadings for both MgO and Mn. The PCA shows that the two most important distinguishing variables in the sediments are carbonate content and clay content.

The associations discussed above can explain the distribution of elements along the length of the vlei. The sediments at De Mond are dominated by $CaCO_3$ and SiO_2 and are enriched in Sr. The highest P_2O_5 concentrations also occur in this area. In the central parts of the vlei the carbonate content decreases, elements associated with clay minerals increase and the sediments are dominated by SiO_2. In the northern parts of the vlei clay minerals and the elements associated with them are dominant. Few patterns of variation in depth in the sediments are evident. Most elements associated with clay minerals are enriched in sub-surface sections due to a clay increase with depth. Carbonate minerals decrease with depth at all sites measured except for T7.

4.4.6 Extractable P, Zn and K

Table 4.7 gives the concentrations of AMBIC extractable P, Zn and K in comparison to the total concentrations in the sediment samples. The extraction method, which involves the use of NH_4HCO_3-NH_4F-$(NH_4)_2$-EDTA, is supposed to give an indication of the availability of these elements to plants growing in soils from which the elements have been extracted. From the results it is clear that these elements occur in the vlei sediments in forms where only a small fraction of the total amount is in an available form.

Table 4.7 The results of extractable P, K and Zn determinations (mg/kg) on selected sediment samples from De Hoop Vlei. The total concentrations determined by XRFS (mg/kg) are given for comparison.

Sample	P		K		Zn	
	Extractable	Total	Extractable	Total	Extractable	Total
M1-90	5.2	340	68.1	2581	1.9	13
M1-255	1.3	336	152.9	9509	2.9	56
H2-110	5.3	265	335.0	12634	1.8	70
W2-170	5.9	229	196.4	17163	1.9	79
W2-250	5.3	202	182.0	16046	2.0	83

Phosphorus in the De Hoop sediments has been identified as probably occurring in association with Ca, either as apatite or co-precipitated with carbonates. This form of P has a low solubility in alkaline environments and therefore a low availability. The values of extractable

P obtained may be compared to values obtained by NH_4HCO_3-DTPA extraction. Values below 3 mg/kg are considered low while values between 4 and 7 mg/kg are considered medium for soils (Olsen and Sommers, 1982). The majority of De Hoop sediment samples can therefore be considered to have medium values of available P. In comparison with values given for Barber's Pan (Knesl, 1996), the total P content of samples from De Hoop Vlei is generally higher but the extractable P values are lower. The values of available P in Barber's Pan are considered high in terms of the values given by Olsen and Sommers (1982). The low availability in De Hoop is to be expected from the probable form of P present.

Phosphorus, Zn and K are all elements that could be introduced into the vlei from fertilizers due to agricultural activities in the catchment. Mechanisms for the removal of these elements from the water with resultant accumulation in the sediments are particularly effective in the vlei environment. It is therefore feasible that sediments in the upper part of the vlei would become relatively enriched in these elements in comparison to sediments in the south of the vlei. This is because inflow waters would undergo interactions with the sediments in the north before reaching those in the south. Also during times of low water such as occurred during the sampling for this study, inflow waters do not reach the southern parts of the vlei as surface flow.

Because of the associations of elements with different components of the sediments it is often not possible to observe enrichment purely by examining concentrations relative to each other. For this purpose it is useful to look at the ratio of an element to another variable which is associated with the particular sediment component in which that element occurs. Because Zn and K are both associated with clay minerals in De Hoop Vlei, the Al to Zn and K ratios were used for this purpose. Although the correlations discussed in the previous section have shown associations between P and CaO, P is not a component of $CaCO_3$ and it is, therefore, not useful to use a ratio related to carbonates. Similarly P is not associated with clay minerals or organic matter in De Hoop Vlei, according to the correlation results. For this reason the P concentrations are used on their own. The variation of the Al/K and Al/Zn ratios and the P concentration with distance along the length of the vlei are plotted for all surface samples in Figure 4.2.

From the figure it is evident that there is a trend of decreasing P concentrations in a northerly direction along the length of the vlei. It can be concluded from this that there is no likely accumulation of P in the sediments in the northern parts of the vlei due to inputs from the Sout River. The K to Al ratio shows a slight trend of increasing northwards suggesting that K is enriched relative to clay content in the northern parts of the vlei. This could be a result

of agricultural contamination. It could, however, also be the result of mica minerals having undergone less alteration in the northern parts of the vlei. The Zn to Al ratio shows no particular trend along the length of the vlei.

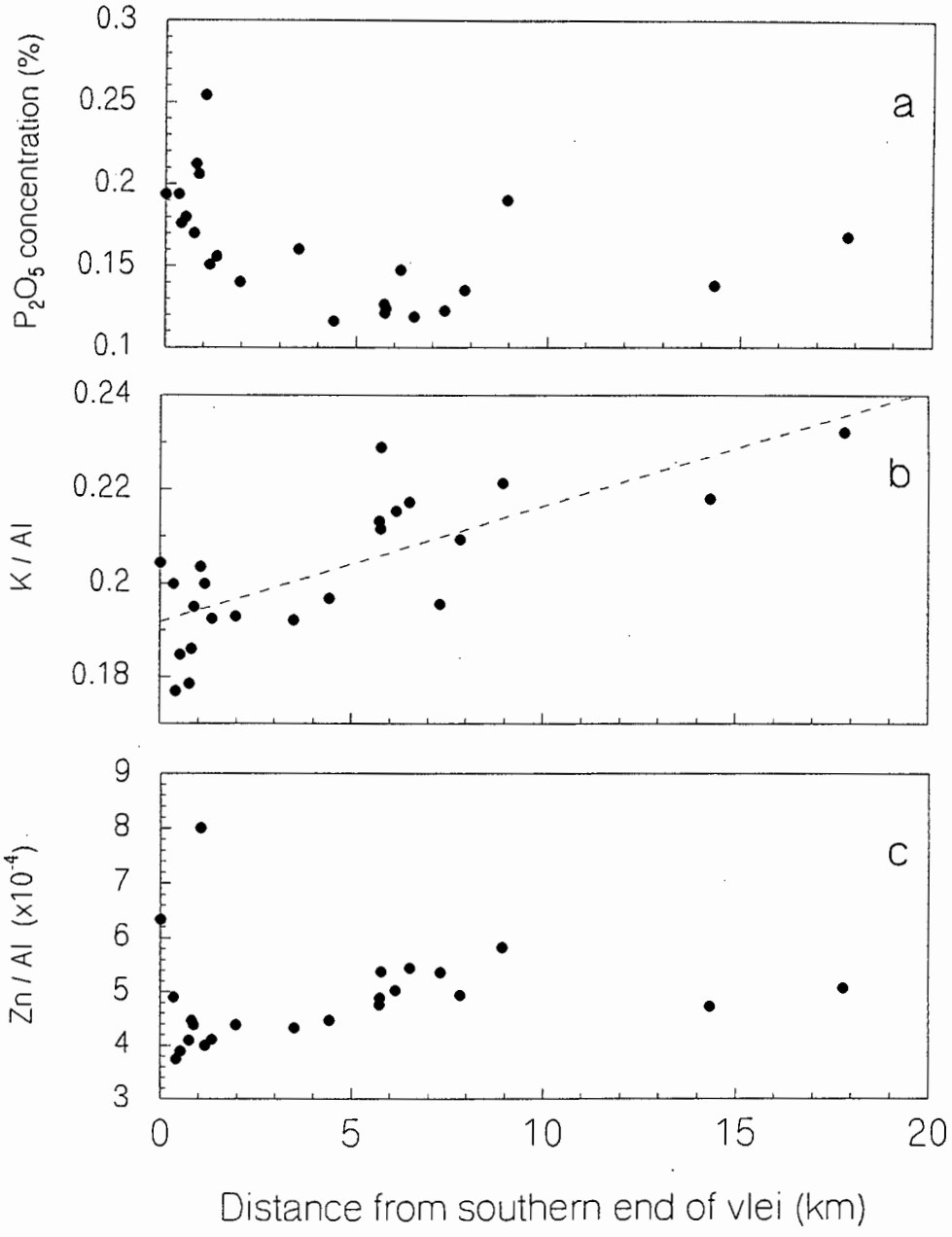

Figure 4.2 The variation in P concentration, and the ratio of K and Zn concentrations to those of Al in all surface samples along the length of De Hoop Vlei. Approximate distances are relative to a line along the centre of the vlei starting at position M5. **a** P_2O_5 (%). **b** K to Al ratio (linear regression: $r^2 = 0.57$; n = 23) **c** Zn to Al ratio.

4.4.7 Mineralogy

The mineralogy of sediments is important for understanding the fate of elements precipitated from the water column and in understanding sediment water interactions, particularly with regard to ion exchange and sorption reactions. In order to understand the mineralogy of different fractions of the De Hoop sediments, a number of different samples were analyzed. The different fractions included the clay fraction, carbonates of the bottom sediments and carbonate secondary precipitates found on boulders and pebbles in the littoral zone. These different fractions are discussed individually below.

4.4.7.1 Mineralogy of clay fraction

The clay fraction, separated from six sediment samples representing a distribution along the length of the vlei and from different depths in the sediment, was analyzed by XRD. The results of this analysis are given in Figure 4.3 which shows the diffractograms from the six samples in comparison to one another. It is evident from these results that the clay mineralogy of the six samples is very similar. It may therefore be concluded that no variation in clay mineralogy exists with depth or along the length of the vlei.

The identification of all peaks in the diffraction patterns were made according to JCPDS (1980) data . The identification of mica in the diffraction patterns can be made by the three peaks at 10.05, 5.01 and 3.34 Å (Fanning *et al.*, 1989). The peak at 2.00 Å may also be attributed to mica. The principal kaolinite peaks are identified at 7.18 and 3.58 Å with a smaller peak at 2.51 Å. The principal quartz peak occurs at 3.34 Å and therefore would be hidden by the mica peak at the same position. However the second strongest quartz peak occurs at 4.26 Å. This peak should have a relative intensity of 35 percent compared to the quartz peak at 3.34 Å. Because the peak at 4.26 Å is so small it can be concluded that very little quartz is present and that the peak at 3.34 Å is predominantly caused by mica.

Unpublished data have shown that the basal peaks of mica and kaolinite have similar relative intensities at similar concentrations (pers com, H. Frimmel). By comparing the intensities of the basal peaks in figure 4.3 it is evident that mica is the dominant clay mineral in the sediment samples. Kaolinite occurs as a sub-dominant clay mineral. The only other mineral occurring in the clay fraction of the sediments is quartz which occurs in trace quantities. The presence of quartz could be a result of the inclusion of some silt into the clay fraction during clay separation or it could be present in the sediments as physically weathered quartz grains of less than 2 μm equivalent diameter.

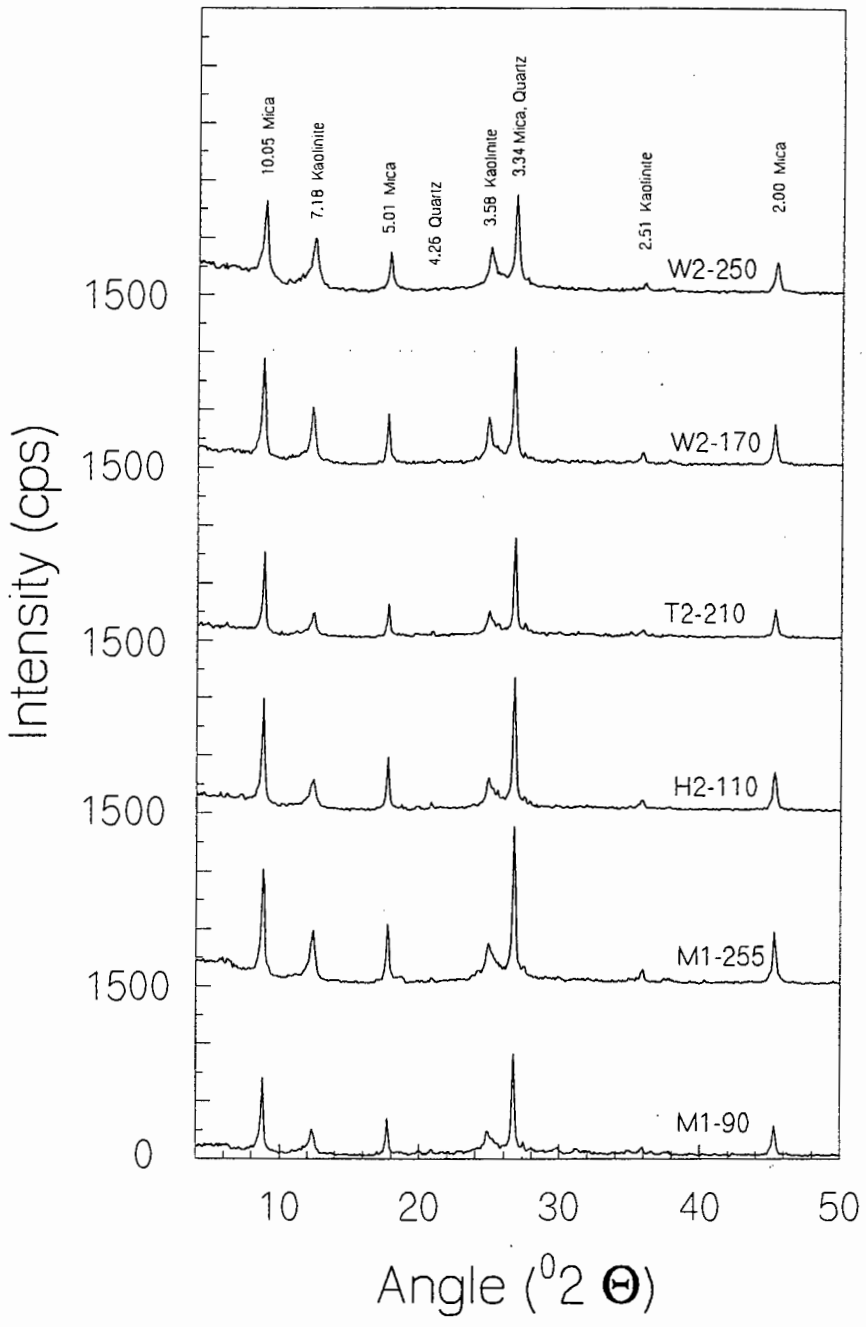

Figure 4.3 X-ray diffraction patterns of the clay fractions of six sediment samples from De Hoop Vlei. The d-spacings of identified peaks are given in Å. Patterns are superimposed on each other with a constant value of 1500 counts per second.

The predominantly micaceous nature of the sediment clays can probably be attributed to the geology and soils of the catchment area. The catchment landscape consists of shallow, poorly weathered soils overlying Bokkeveld shales (see Chapter 1) which have a high content of micaceous minerals (Truswell, 1977). The potential for erosion and transport by surface

waters of clays consisting predominantly of primary micaceous minerals is, therefore, high. The sub-dominant clay mineral type is kaolinite, which commonly occurs in abundance in many soil types (Allen and Hajek, 1989).

The sediment clays are, therefore, likely to be derived directly from the soils and rocks of the catchment. No evidence of clay mineral formation or alteration in the vlei is shown by the XRD data. It should be noted, however, that minerals present in a quantity of less than approximately 5 percent of the total clay will not be detected by an XRD analysis (Whittig and Allardice, 1986). If secondary clay formation has occurred, therefore, it has not done so to a large extent.

4.4.7.2 Mineralogy of whole sediment

In order to investigate the mineralogy of the carbonates present in the vlei sediments, a sample with high carbonate content, M8, was analyzed by XRD. The analysis was performed on the bulk sample without separation of any fractions. The result of this analysis is given in Figure 4.4.

Three different minerals were identified in this sample. These were quartz, calcite and aragonite. Comparisons were made by van der Spuy and Willis (1991) of the relative intensities of calcite and aragonite peaks. The calcite peak at 3.03 Å had an intensity of approximately 17 times that of the aragonite 2.71 Å peak when the same percentage of the two minerals were compared. From the intensities of the peaks in Figure 4.4, it appears that the sediment is dominated by quartz and aragonite with lesser amounts of calcite present. Using the relative peak intensities of van der Spuy and Willis, there is approximately 3.5 times as much aragonite present as there is calcite. High quartz is to be expected as it is the principal component of the sand fraction. The high aragonite and calcite content is evidence that carbonates are a major sink for Ca in the De Hoop Vlei. The identified mineralogy agrees with saturation indices calculated for the water samples which were supersaturated with respect to both calcite and aragonite. Aragonite is likely to be associated with the shells of organisms, which were observed in the sediment samples.

All the peaks in Figure 4.4 can be attributed to one of the three minerals. It can therefore be concluded that no other minerals are present in significant quantities. The low clay content of the sample results in clay minerals not being detected due to dilution by carbonates and quartz. It is also interesting that the carbonate minerals, monohydrocalcite and nesquehonite which were identified in precipitates from the littoral zone (see following section) are not

detectable in this bottom sediment sample.

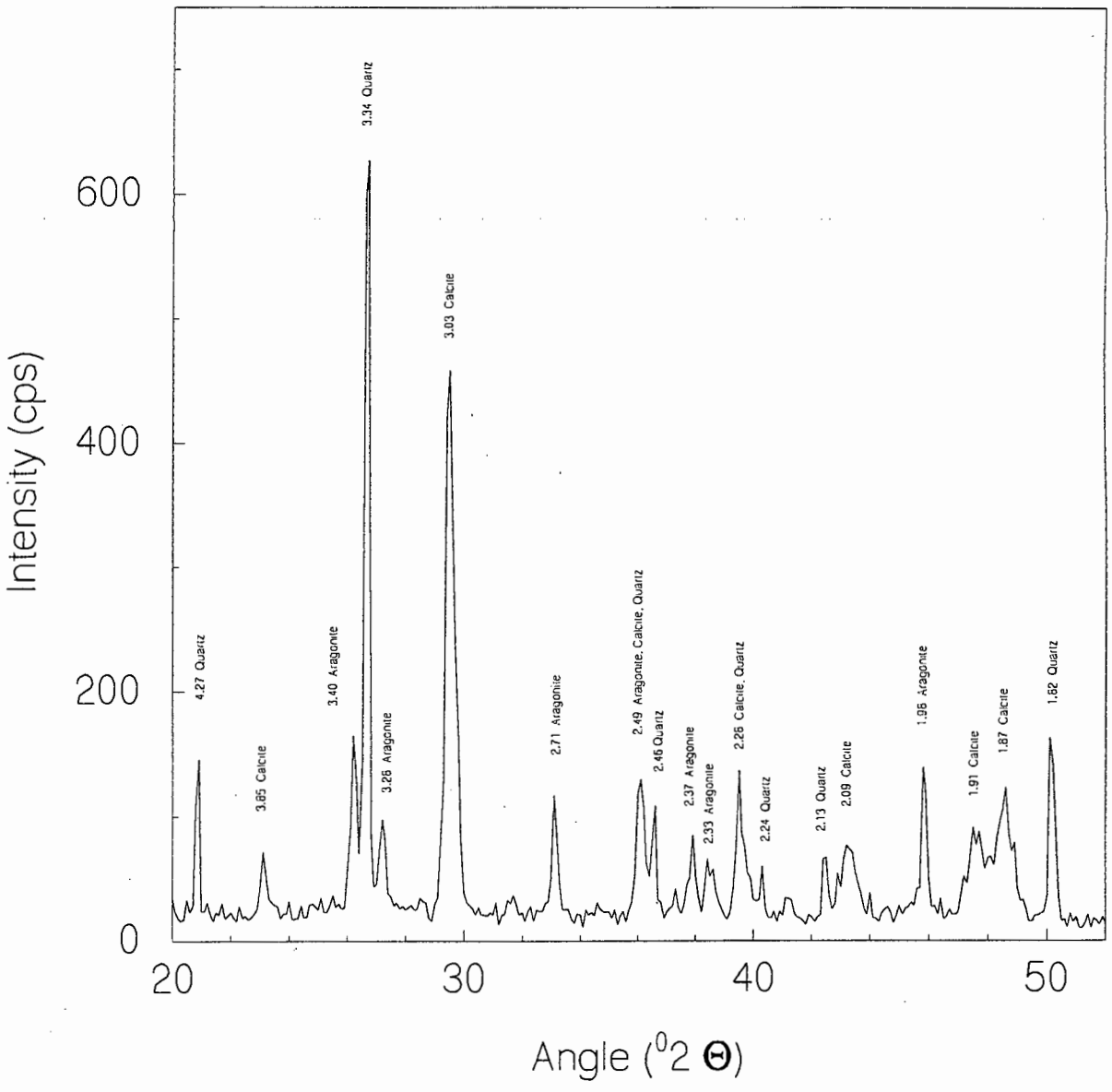

Figure 4.4 X-ray diffraction pattern of the bottom sediment sample, M8-160 from De Hoop Vlei. The bulk sediment was used for analysis without the separation of any fractions. All d-spacings are given in Å.

4.4.7.3 Mineralogy of secondary precipitates

A layer of white precipitates was identified on the boulders along the edge of the vlei. This occurred on all the boulders of the limestone cliffs running along the eastern edge of the vlei

to the south of the De Hoop homestead. The precipitate occurred from below the water level that existed at the time of sampling to a height of approximately 3 metres above it. The precipitate was a relatively soft, white material that could be easily scraped from the underlying stone. The precipitate close to the waters edge was softer than that which existed higher up. It had an extremely rough surface that had indentations of up to approximately 3 mm in depth. A photograph of the cliffs in the De Mond area which shows the precipitate is given in Figure 4.5.

It was initially uncertain whether the surface texture was the result of precipitation or of dissolution of the limestone. However, the discovery of quartzitic pebbles from the water's edge, which were covered by the same surface, confirmed that it was probably the result of precipitation. Samples of the precipitate were reacted with concentrated HCl. The strong effervescence that resulted confirmed that the precipitate is a carbonate.

Two samples of the precipitate collected from different places were analyzed by XRD. The one sample was taken from the limestone boulders at sampling site M6. This sample is numbered PrM6. The other occurs on the surface of one of the quartzitic pebbles which was collected at the waters edge on a small beach at the edge of the vlei from site D2. A photograph of the pebble is given in Figure 4.6. The sample is numbered PrD2. The results of XRD analyses for the two samples are compared in Figure 4.7.

Four different minerals are identified from the XRD pattern of sample PrD2. These are monohydrocalcite ($CaCO_3.H_2O$), nesquehonite ($MgCO_3.6H_2O$), calcite and aragonite. The presence of monohydrocalcite is evident from the strong peak at 4.33 Å. Several other strong peaks for this mineral are also clearly evident. The presence of nesquehonite is evident from the strong peak at 6.51 Å. Several of the other nesquehonite peaks overlap with those of calcite including the two strongest calcite peaks at 3.03 and 3.85 Å. The contribution of calcite causes an increase in the intensities of these peaks so that their intensity relative to the strongest nesquehonite peak at 6.51 Å is higher than it would be for pure nesquehonite. The strongest aragonite peak occurs in isolation at 3.41 Å. From the XRD pattern it appears that the sample is dominated by monohydrocalcite and nesquehonite with smaller quantities of calcite and aragonite, although the relative intensities of the peaks produced by the different minerals is not known. No other minerals are evident. The XRD pattern of sample PrM6 is essentially the same, except that nesquehonite is completely absent from this sample.

Both monohydrocalcite and nesquehonite are unusual minerals and their occurrence is reported very infrequently in the literature. A comprehensive search for monohydrocalcite in

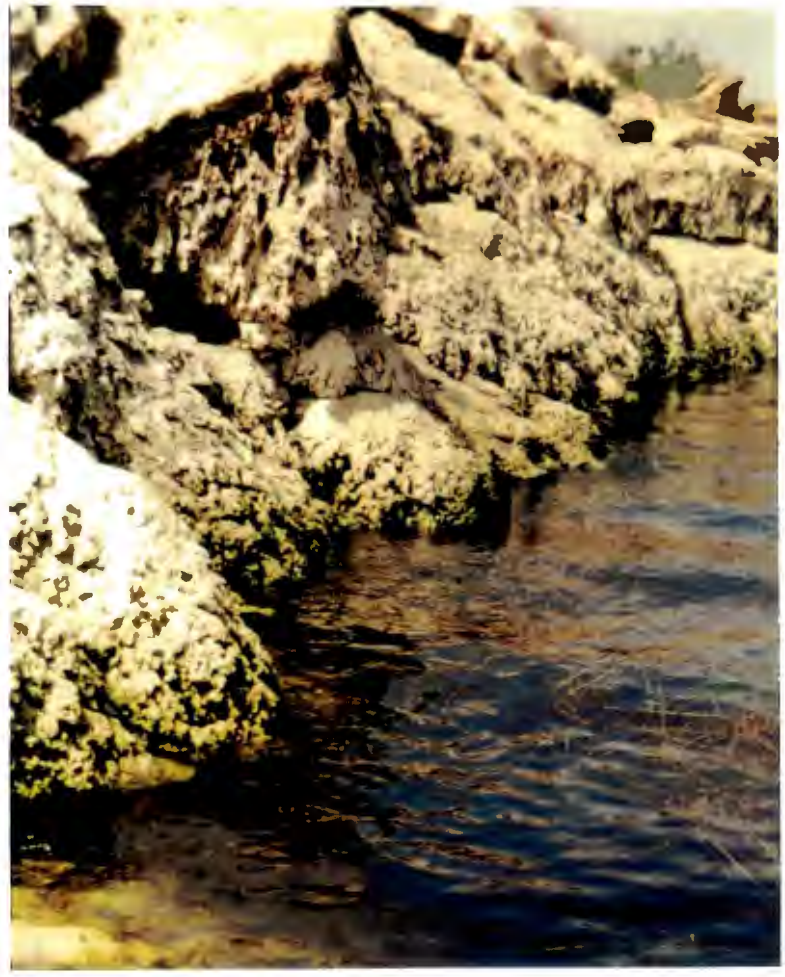

Figure 4.5 A photograph of the cliffs from which the precipitate sample, PrM6 was taken. The uneven surface of the precipitate, covering rock surfaces up to approximately 2 metres above the water level, is clearly visible.

Figure 4.6 Photograph of a pebble from the littoral zone of the southern part of De Hoop Vlei showing the white precipitate which covered the upper surface of the pebble. The sample PrD2, which was analyzed by XRD and SEM, was taken from this precipitate. The diameter of the pebble is 7 cm.

Chemical Abstracts produced only a few references to this mineral. Last and De Deckker (1990) state that it has only rarely been identified in natural environments. Its natural occurrence was first reported in the sediments of a saline lake (Hull and Turnbull, 1973). Subsequently it has been reported in the sediments of Lake Fellmongery in South Australia (Hull and Turnbull, 1973) and of Lake Sevan in the USSR where it occurred with low Mg and high Mg calcite (Reznikov and Turovskii, 1983). More recently it has been identified in carbonate hardgrounds from East Basin Lake, a saline maar lake in southern Australia. It occurred on its own in a finely crystalline form as a surface layer on microbialites (biologically mediated carbonate rocks) (Last and De Deckker, 1990; Last 1992). It was not, however, present in a neighbouring lake and the authors were unable to offer an explanation for its occurrence in East Basin Lake. They stated that in each previously reported occurrence of lacustrine monohydrocalcite, the precipitating waters have been characterised by moderate Mg/Ca ratios and salinity. Last (1992) also states that the absence of aragonite in the microbialites refutes the hypothesis that monohydrocalcite is unstable and rapidly transforms to aragonite in Na-Cl rich brines.

Monohydrocalcite has been precipitated from sea water in laboratory studies, in one case with sodium carbonate (Hull and Turnbull, 1973). It also occurred as less than 1 percent of the carbonates precipitated in a study of carbonate precipitation by *Bacillus* species in saline media (Rivadeneyra *et al.*, 1994).

Nesquehonite has been reported as occurring in efflorescent crusts in saline lakes in Canada (Renaut, 1990) and in evaporative rocks in saline lakes in Tibet (Zheng and Yang, 1983). It has also been identified as white efflorescences of weathering origin on Antarctic stone meteorites (Velbel *et al.*, 1991). The occurrence of nesquehonite in precipitates together with monohydrocalcite has not been previously reported.

From the XRD results discussed above, it would appear that monohydrocalcite is the principal form of $CaCO_3$ being precipitated in the littoral zone of the southern part of De Hoop Vlei, at least in association with the surfaces of rocks. The reason for the precipitation of monohydrocalcite rather than calcite is unknown. The waters of De Hoop are, however, similar to waters where it has previously been identified in terms of a moderate Mg/Ca ratio and salinity. In East Basin Lake where it occurred the waters were also dominated by Na and Cl (Last and De Deckker, 1990).

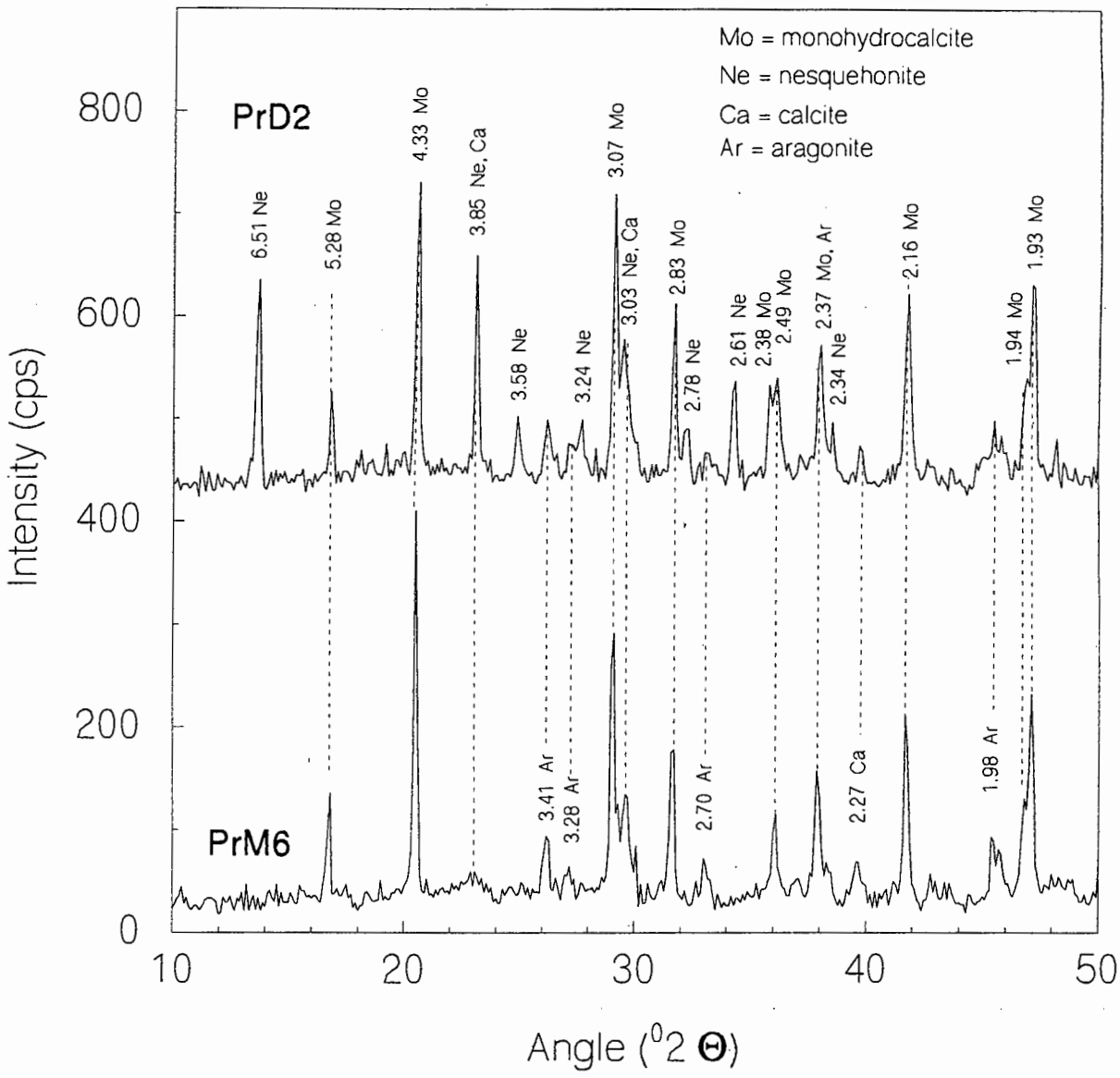

Figure 4.7 X-ray diffraction powder pattern of two secondary precipitate mineral samples from rock surfaces in the littoral zone of De Hoop Vlei. The pattern of sample PrD2 is superimposed on a value of 400 counts per second. All d-spacings are given in Å.

Some factors which may influence the precipitation of monohydrocalcite are referred to in previous studies. Hull and Turnbull (1973) concluded from their study that thermochemical evidence suggests that monohydrocalcite forms from solutions as a metastable precipitate when the presence of Mg or polyphosphates kinetically inhibits the formation of calcite. Previous studies had noted that the transformation of monohydrocalcite to aragonite, which occurs in water, is prevented by small amounts of either Mg or polyphosphates in solution

(Hull and Turnbull, 1973). Monohydrocalcite precipitated from sea water in the laboratory was stable in its mother liquor, but slowly changed to calcite or aragonite when dry (Hull and Turnbull, 1973). The presence of small amounts of oxalate anions in solution has also been found to favour the formation and stabilization of monohydrocalcite (Efthimios and Koutsoukos, 1988). Rivadeneyra *et al.* (1994) in a study under saline conditions showed that bacteria play a direct role in the precipitation of $CaCO_3$ and that the type of bacteria involved has an effect on the kind of $CaCO_3$ precipitated. The precipitation of monohydrocalcite in De Hoop may, therefore, be due to a biological influence.

The precipitation of nesquehonite has been found to be influenced by the presence of NaCl. In a study on nesquehonite efflorescence on the surface of polishing bricks, Decastellar *et al.* (1996) found that calcite nucleation was inhibited by the presence of halite, and only nesquehonite precipitated in samples where halite was present. The high Na and Cl concentrations in De Hoop may therefore play a role in nesquehonite precipitation.

4.4.7.3.1 Morphology and chemistry of secondary precipitate minerals

Because of the interesting mineralogy of sample PrD2 it was investigated further using scanning electron microscopy (SEM) in conjunction with energy dispersive XRFS. SEM images of the precipitate are given in Figure 4.8. At low magnification the images reveal the very uneven surface of the precipitate (Figure 4.8a). Desiccation cracks in the surface are visible at centre right in this image and in 4.8b. At higher magnification a matrix containing roughly circular clusters of elongated crystals is visible in an arrangement where their long axis points to the centre (4.8c and d). The crystals show possible evidence of dissolution (4.8e). A high magnification image of these crystals is shown in Figure 4.8f. No crystal structure was evident in the matrix even at high magnification (4.8b) but it showed an intricately indented morphology giving rise to a high porosity. The surface of the precipitate appeared to be coated with a layer of the fine grained material. Figure 4.8g shows the broken edge of the precipitate layer with the coated outside surface and complex morphology with high porosity below.

Spot analyses of certain parts of the sample using EDXRFS revealed differences in the chemical composition of different structures. Three spectra are given in Figure 4.9. A spectrum of the elongated crystals showed them to be high in Mg and O with very low Ca and they were therefore identified as nesquehonite. The crystal morphology is similar to that revealed in images of nesquehonite crystals discussed by Velbel *et al.* (1991). The spectrum obtained from the matrix material was high in Ca with low Mg, and less O than the spot

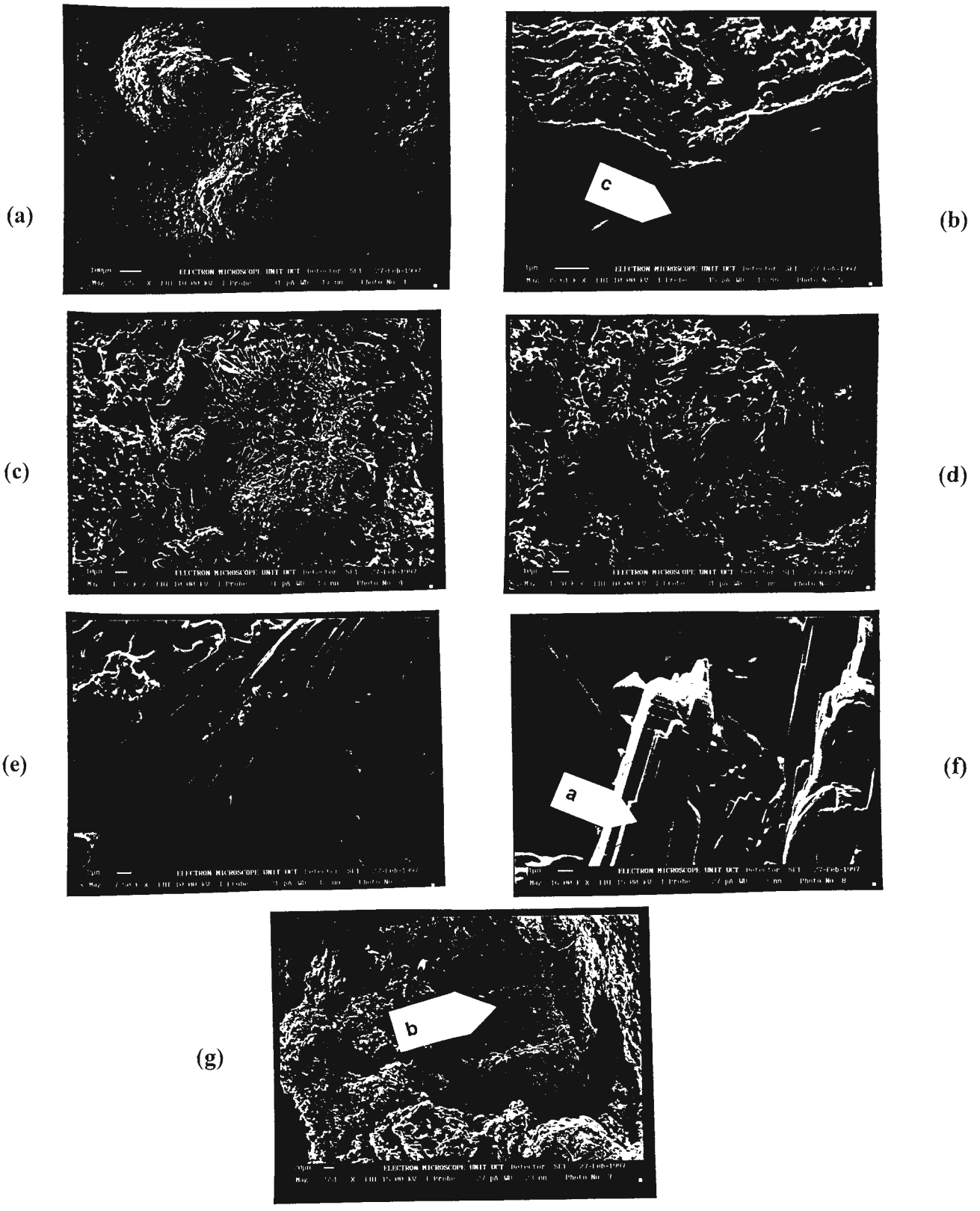

Figure 4.8 Scanning electron microscope (SEM) images of secondary precipitate sample PrD2 from the littoral zone of De Hoop Vlei. **a** surface of the precipitate at low magnification; **b** desiccation crack at high magnification; **c, d** clusters of elongated nesquehonite crystals; **e** possible signs of dissolution on crystals; **f** high magnification image of nesquehonite crystals; **g** broken edge of the precipitate layer. The letters a,b and c on the images indicate the positions at which the spot analyses shown in Fig. 4.9 were done.

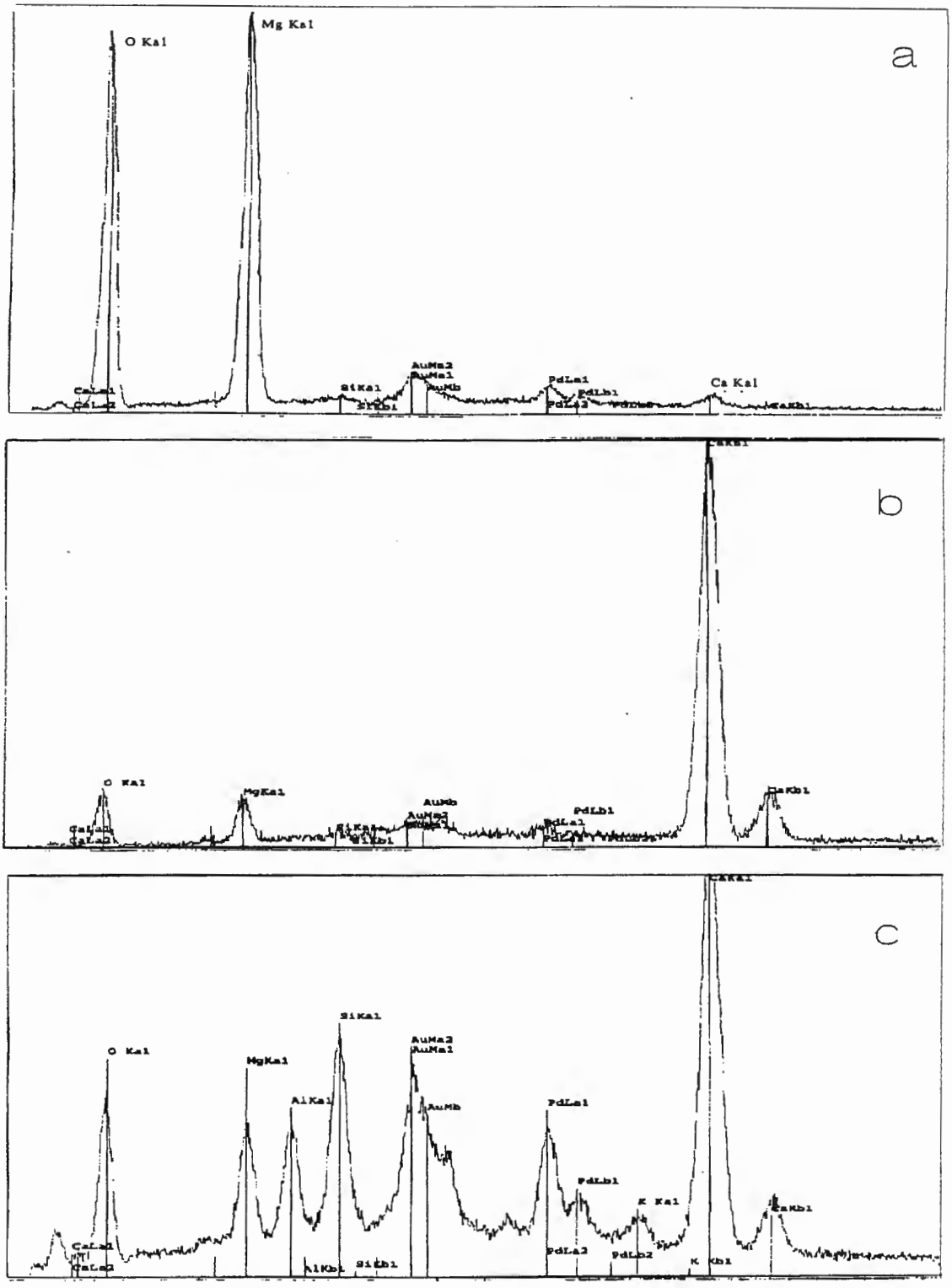

Figure 4.9 Spectra produced by spot analysis of secondary precipitate sample PrD2 using energy dispersive XRFS. **a** nesquehonite crystals **b** matrix of monohydrocalcite **c** surface coating on precipitate. The positions at which spot analyses were done are shown in Fig. 4.8.

analysis of nesquehonite crystals. This material was therefore identified as monohydrocalcite crystals. A spectrum of the smooth coating indicated a high Ca concentration as well as high Mg and moderately high O, Si, Al, and some K. This material could therefore be a combination of monohydrocalcite and nesquehonite. No other source of a high Mg concentration is evident from the XRD results. Clay mineral impurities could explain some Mg and the Si, Al and K. The Au and Pd peaks are a result of the coating applied during sample preparation.

From the analyses performed on the precipitate it can be concluded that it consists of a matrix of very finely grained, porous monohydrocalcite with clusters of larger nesquehonite crystals imbedded in the matrix. Some clay mineral impurities occur in low concentrations.

4.5 Conclusions

Four major components of the De Hoop sediments were identified in this study. These were carbonate minerals, resistate minerals of sand-and silt size, clay minerals and organic matter. The proportions of these vary along the length of the vlei. A significant quantity of the carbonate minerals are likely to result from the transfer of dissolved Ca and carbonates from the water column to a solid phase in the sediments. Some carbonates are also likely to be the result of aeolian transport of dune sands while both resistate and clay minerals are likely to have been deposited by water and wind transport.

Sediments in the south of the vlei at De Mond are dominated by carbonate minerals. The dominant carbonate mineral was found to be aragonite with lesser amounts of calcite. These minerals are likely to be controlling Ca concentrations in the waters of De Hoop Vlei. The amount of $CaCO_3$ present suggests that significant quantities of Ca and carbonate are being lost from the water column in the De Mond area. In the littoral zone, secondary precipitates of two unusual carbonate minerals, monohydrocalcite and nesquehonite were identified. In association with rock surfaces in this area, these minerals precipitate instead of calcite or aragonite. The reason for this is unknown. In one of the samples analyzed, monohydrocalcite and nesquehonite occurred in association with each other. Nesquehonite is present as clusters of large, elongated crystals within a porous matrix of fine grained monohydrocalcite. Elements associated with the carbonate fraction in the De Hoop sediments are Ca, Sr and P. Carbonate minerals generally decrease with depth in the sediments.

The resistate mineral component consists predominantly of quartz. It is likely that Zr in the form of zircon also occurs in this fraction although no correlation between Zr and SiO_2

existed in the samples. The proportion of the sand and silt component increases in a northerly direction along the length of the vlei.

The clay mineral content of the sediments increases markedly in a northerly direction along the length of the vlei. No sorting effects were evident across the width of the vlei. Clay content generally increases with depth in the sediments. The only clay minerals identified in the samples were micas which are dominant in the clay fraction and kaolinite, which occurs in smaller amounts. Both these minerals are likely to be derived directly from the soils and rocks of the catchment. The mineralogy of the clay fraction along the length of the vlei and at different depths in the sediment was found to be almost identical. Concentrations of Al, Fe, Ti and K and the trace elements Ba, Rb, V, Cr, Zn, Ni, Y, Pb, Sc, Co, Nb, and Th showed strong positive correlations with clay percentage and are therefore likely to occur almost exclusively in the clay mineral fraction of the sediments. There is no evidence of an association of trace metals with carbonates or organic matter.

Magnesium is probably associated with both carbonates and with clay minerals. In the southern part of the vlei it is probably present as magnesium carbonate minerals, while in the north, where the clay content is high and carbonates are low, most magnesium is likely to be associated with clay minerals.

The elements most strongly associated with the organic matter fraction are S and U. No pattern in the spatial variation of organic matter content was found, although organic matter content is generally lower in the northern Windhoek region than further south.

The accumulation of P, K and Zn, which are all potentially augmented by agricultural activities, was compared in sediments in the southern and northern parts of the vlei to give an indication of any enrichment due to agricultural contamination. There was a trend of decreasing P concentrations in a northerly direction along the length of the vlei which showed that there is no likely accumulation of P in the sediments in the northern parts of the vlei due to inputs from the Sout River. Some K enrichment could, however, be occurring in the northern parts of the vlei. No similar enrichment in Zn was evident in the samples. From these results there is no clear indication of any agricultural contamination. Only a small fraction of the total amount of P, K and Zn was found to be extractable in ammonium bicarbonate. The low solubility of these elements means that their concentrations are unlikely to reach high levels in the water column.

Reducing conditions in much of the sedimentary environment of De Hoop Vlei was evident

in that sediment material changed from a black colour to light brown upon exposure to air. The colour change was ascribed to the presence of iron monosulphide minerals in the sediments. All samples except those from the Rietkloof and Windhoek areas in the north of the vlei showed this behaviour. The acidifying effect from the oxidation of the sulphide minerals upon drying of the sediments was found to be unimportant in the De Hoop Vlei environment. Reducing conditions were found to result in a lowering of the pH.

This study of the geochemistry of the De Hoop sediments has shown considerable variation in the vlei. Sediments are either high in $CaCO_3$ or in clay minerals and these components largely control the elemental composition of the sediments. Much of the sedimentary environment is subject to reducing conditions. The sediments have been shown to play an important role in the water chemistry of the vlei, particularly with regard to precipitation/dissolution, sorption and redox reactions. Chemical sedimentation is likely to be occurring from the water column and the sediments are probably a sink for many elements introduced by river inflow to the vlei.

Chapter 5 Conclusions

The objectives of this study were outlined in a number of key questions posed in the introduction. Answers to these questions, based on the findings of the study, are presented in this chapter.

- **What geochemical factors and processes control the water chemistry of De Hoop Vlei?**

De Hoop Vlei is a hydrologically closed basin and the water chemistry is, therefore, influenced by the composition of the influent waters as well as by geochemical processes that occur during evaporative concentration of the vlei water. Two types of water, which differ in their chemical composition, were identified as influent water to De Hoop Vlei. The first type includes the water of the Sout and Potberg Rivers, which flow into the northern part of the vlei. The second type is water of the Tierhoek Spring. These waters differ in terms of salinity as well as major ion chemistry. The Tierhoek water can be considered fresh, with a salinity of around 0.5 g/L, while those of the catchment are saline with salinity values of up to 16 g/L. The Tierhoek water also has much higher proportions of Ca and carbonates than those of the rivers.

It is likely that a high proportion of the salinity in the influent water originates from the sea and is transported into the catchment through wet and dry deposition. This is evident from the high Na and Cl dominance of all waters of the catchment, including those not directly affected by evaporative concentration.

The water chemistry of De Hoop Vlei is characterised by a high degree of spatial and temporal variation. Much of the spatial variation is explained by the source of the water in a particular part of the vlei and the mixing of the two water types. Mixing reduces the salinity of the river water in the vlei and introduces higher concentrations of Ca and carbonates.

The water chemistry is also influenced by evaporative concentration, with water in the south of the vlei being the most affected because it remains there as surface water during dry periods. Evaporative concentration increases the salinity of the water and changes the chemical composition. A significant quantity of $CaCO_3$ is lost from the water column during evaporative concentration and transferred to the sediments. As a result of this, Ca is depleted and the pH of the water increases to a value of approximately 10.

During evaporative concentration, all major solutes, including Na, are lost from the water column relative to chloride to varying extents. Non-conservative behaviour is unusual for Na and can possibly be explained in De Hoop Vlei by stripping of Ca and Mg from exchange sites due to their precipitation as carbonates, which enables Na to exchange for these cations on exchange sites in the sediments. It is likely that loss of Mg is due to precipitation of Mg carbonate minerals. The De Hoop waters become supersaturated with respect to a number of Ca and Mg carbonates including calcite, aragonite, monohydrocalcite and nesquehonite as well as *sepiolite*. The solubility of these minerals is likely to control the dissolved concentrations of Ca and Mg. The two minerals, monohydrocalcite and nesquehonite, which were identified as secondary precipitates in De Hoop Vlei, are rare and their natural occurrence has been reported very infrequently in the literature.

There is evidence of SO_4 reduction in the sediments of De Hoop. This is likely to be the main mechanism by which SO_4 is removed from the water column. Potassium removal in De Hoop Vlei, probably by adsorption on clay minerals, is very effective and K is removed to a large extent during evaporative concentration.

- **To what extent is the water chemistry buffered against changes?**

The high alkalinity of the De Hoop Vlei waters and the high carbonate content in the sediments means that the system is very effectively buffered against changes in pH. Introductions of acidity, for example through atmospheric deposition, would have little effect on the water chemistry of De Hoop.

The introduction of low salinity water from Tierhoek and other springs buffers an increase in salinity to a certain extent. However, a long term reduction in the volume of inflow from the rivers is likely to result in lower water levels and increased salinity in the vlei.

The concentrations of a number of solutes are buffered during evaporative concentrations due to saturation and, therefore, equilibrium with a solid phase. The levels of these solutes can theoretically not exceed equilibrium concentrations. This applies to a number of major solutes as well as trace metals and P concentrations, which are considered in more detail in answering the final key question.

- **Is there evidence of agricultural contamination in the vlei or in the waters of the catchment?**

Results have shown that high phosphate levels occur periodically in the catchment waters. In

some samples analyzed for this study, particularly high phosphate levels, which were far in excess of average concentrations, were measured. It is possible that they are the result of fertilizer contamination of runoff. No elevated nitrate or trace metal concentrations were detected in surface water samples. Analyses were not done for pesticides.

The concentration of P, K and Zn in the sediments from different depths and from different parts of the vlei show no evidence of P and Zn contamination. The K to Al ratio shows some evidence of being higher in the upper vlei relative to the southern parts. This is, however, likely to be the result of factors associated with K adsorption by clay minerals and not the result of agricultural contamination.

• What is the fate of possible contaminants in the system and would they have the potential to affect the ecology of the vlei ?

The results of the P analyses in surface waters suggest that P enrichment of surface waters is possibly occurring in the catchment but that it is effectively being removed from the water column in the vlei. Geochemical modelling showed that P has a low solubility in the vlei water and it may, therefore, be buffered at low concentrations by equilibrium with an apatite solid phase in the sediments. Alternatively, the low concentrations of P in the vlei water may be the result of uptake by aquatic organisms.

Geochemical modelling of hypothetical Zn and Pb contamination in the waters of De Hoop Vlei showed that these elements also would have extremely low solubility, which is likely to be controlled by equilibrium with solid phases in the sediments. Another possible indication from geochemical modelling, which has bearing on the ecological effects of contaminants, is that most potentially toxic elements are present in the water in species other than their free ions. This may possibly reduce the ecological effects of an introduction of these elements as contaminants into the waters of the vlei.

References

Aladin, N. V. and I. S. Plotnikov. 1993. Large saline lakes of former USSR: a summary review. *Hydrobiologia* 267:1-12.

Allen, B.L. and B.F. Hajek. 1989. Mineral occurrence in soil environments. In Dixon, J.B. and S.B. Weed (eds). Minerals in Soil Environments (2nd edition). Soil Science Society of America, Madison.

Alloway, B.J. 1995. Heavy metals in soils (2nd edition). Blackie Academic and Professional.

Aston, S. R. and R. Chester. 1976. Estuarine sedimentary processes. In Burton, J.D. and P. S. Liss (eds). Estuarine Chemistry. Academic Press, London.

Ben-Yaakov, S. 1973. pH buffering of pore water of recent anoxic marine sediments. *Limnology and Oceanography* 18:86-94.

Birch, G.F. 1981. The Karbonat-Bombe: a precise, rapid and cheap instrument for determining calcium carbonate in sediments and rocks. *Transcripts of the Geological Society of South Africa* 84:199-203.

Burton, J. D. 1976. Basic properties and processes in estuarine chemistry. In Burton, J.D. and P. S. Liss (eds). Estuarine Chemistry. Academic Press, London.

Butcher, S. E. 1983. Environmental factors and the water regime of De Hoop Vlei. Unpublished M.Sc. thesis. University of Cape Town.

Camur, M.Z. and H. Mutlu. 1996. Major-ion geochemistry and mineralogy of the Salt Lake (Tuz Gölü) basin, Turkey. *Chemical Geology* 127:313-329.

Castanier, S., M. Berner-Rollande, A. Maurin and J. Perthuisot. 1993. Effects of microbial activity on the hydrochemistry and sedimentology of Lake Logipi, Kenya. *Hydrobiologia* 267:99-112.

Clavero, V., J.A. Fernandez and F.X. Niell. 1990. Influence of salinity on the concentration and rate of interchange of dissolved phosphate between water and sediment in Fuente Piedra lagoon (S. Spain). *Hydrobiologia* 197:91-97.

Coetzee, D. J. 1986. Zooplankton and some environmental conditions in De Hoop Vlei, a southern Cape coastal lake. *Bontebok* 5:10-16.

Comin, F.A. and W.D. Williams. 1994. Parched continents: our common future. In Margalef, R. (ed). Limnology now: a paradigm of planetary problems. Elsevier Science, Amsterdam.

Cotter-Howells, J.D. and E. Outram. 1997. Correlations between free metal ion concentration and ecotoxicity in soil solutions. Proceedings of the Society for Environmental Geochemistry and Health 15th European conference on Mining and the Environment. Dublin.

Day, J. A. 1993. The major ion chemistry of some southern African saline systems. Hydrobiologia 267:37-59.

Decastellar, M.D., A. Traveria, J.M. Tura and J.C. Lorente. 1996. Nesquehonite efflorescence on the surface of polishing bricks and calcite nucleation inhibition as an effect of high halite concentration. *Neues Jahrbuch fur Mineralogie-Monatshefte* 8:337-343.

Department of Water Affairs and Forestry. 1993. South African Water Quality Guidelines. Department of Water Affairs and Forestry, Pretoria.

Doner, H.E. and W.C. Lynn. 1989. Carbonate, halide, sulfate, and sulphide minerals. In Dixon, J.B. and S.B. Weed (eds). Minerals in Soil Environments (2nd edition). Soil Science Society of America, Madison.

Drever, J.I. 1988. The Geochemistry of Natural Waters. Prentice Hall, New Jersey.

Dunbar, G. 1996. A report on the state of the water chemistry of the De Hoop Vlei since 1965, and the comparison of the water chemistry of two sites in this vlei with that of Die Dam for 1996. Unpublished Research Report, University of Cape Town.

Efthimios, K. and P.G. Koutsoukos. 1988. Precipitation of calcium carbonate in aqueous solutions in the presence of oxalate anions. *Chemical Abstracts* 109:61931.

Eugster, H.P. 1980. Geochemistry of evaporitic lacustrine deposits. *Annual Review of Earth and Planetary Sciences* 8:35-63.

Eugster, H.P. and B.F. Jones. 1979. Behaviour of major solutes during closed-basin brine evolution. *American Journal of Science* 279:609-631.

Evans, J.C. and E.E. Prepas. 1996. Potential effects of climate change on ion chemistry and phytoplankton communities in praire saline lakes. *Limnology and Oceanograohy* 41:1063-1076.

Fanning, D.S., V.Z. Keramidas and M.A. El-Desoky. 1989. Micas. In Dixon, J.B. and S.B. Weed (eds). Minerals in Soil Environments (2nd edition). Soil Science Society of America, Madison.

Fanning, D.S., M.C. Rabenhorst and J.M. Bigham. 1993. Colors of acid sulfate soils. In Bigham, J.M. and E.J. Ciolkosz (eds). Soil Color. Soil Science Society of America, Madison.

Forstner, U. and G.T.W. Wittman. 1979. Metal Pollution in the Aquatic Environment. Springer-Verlag, Berlin.

Garcia, C. M. and F. X. Niell. 1993. Seasonal change in a saline temporary lake. *Hydrobiologia* 267:211-223.

Gibbs, R.J. 1970. Mechanisms controlling world water chemistry. *Science* 170:1088-1090.

Graham, M.C., J.G. Farmer and A.B. Mackenzie. 1997. Metal biogeochemical behaviour in the saltmarsh environment. Proceedings of the Society for Environmental Geochemistry and Health 15th European conference on Mining and the Environment. Dublin.

Hamilton-Taylor, J. and W. Davison. 1995. Redox - driven cycling of trace elements in lakes. In Lerman, A., D. M. Imboden and J. R. Gat (eds). Physics and Chemistry of Lakes. Springer-Verlag, Berlin.

Hammer, U. T. 1986. Saline lake ecosystems of the world. Dr W. Junk Publishers, Dordrecht.

Harck, T.R. 1994. A geochemical investigation of the aquatic sediments, groundwater and surface water of the Verlorenvlei coastal lake, with special reference to nitrate transformations. Unpublished M.Sc. thesis. University of Cape Town.

Hull, H.S. and A.G. Turnbull. 1973. A thermochemical study of monohydrocalcite. *Geochimica et Cosmochimica Acta* 37:685-694.

Idso, S.B. 1973. On the concept of lake stability. *Limnology and Oceanography* 18:681-683.

JCPDS. 1980. Mineral Powder Diffraction File, Search Manual.

Kilham, P. and P.L. Cloke. 1990. The evolution of saline lake waters: gradual and rapid biogeochemical pathways in the Basotu Lake District, Tanzania. *Hydrobiologia* 197:35-50.

Knesl, O. 1996. A Geochemical Investigation of the Waters and Sediments of Barber's Pan, North West Province. Unpublished M.Sc. thesis. University of Cape Town.

Larsen, J., J.F. Boyle and H.J.B. Birks. 1996. Variation in the geochemistry of recent lake-sediments along a west-east pollution gradient in the Bergen Area, Norway. *Water Air and Soil Pollution* 88:47-81.

Last, W.M. 1992. Petrology of modern carbonate hardgrounds from East Basin Lake, a saline maar lake, southern Australia. *Sedimentary Geology* 81:215-229.

Last, W.M. 1993. Geolimnology of Freefight Lake: an unusual hypersaline lake in the northern Great Plains of western Canada. *Sedimentology* 40:431-448.

Last, W.M. and P. De Deckker. 1990. Modern and Holocene sedimentology of two saline volcanic maar lakes, southern Australia. *Sedimentology* 37:967-981.

Lerman, A. and B.F. Jones. 1973. Transient and steady state salt transport between sediments and brine in closed lakes. *Limnology and Oceanography* 18:72-85.

Lewis, W.M., J.F. Saunders, D.W. Crumpacker and C.M. Brendecke. 1984. Eutrophication and land use. Ecological Studies 46. Springer-Verlag, New York.

Lijklema, L. 1994. Nutrient dynamics in shallow lakes: effects of changes in loading and role of sediment-water interactions. *Hydrobiologia* 275:335-348.

Liss, P.S. 1976. Conservative and non-conservative behaviour of dissolved constituents during estuarine mixing. In Burton, J.D. and P. S. Liss (eds). Estuarine Chemistry. Academic Press, London.

Lowenstein, T.K. and L.A. Hardie. 1985. Criteria for the recognition of salt pan evaporites. *Sedimentology* 32:627-644.

Mackenzie, F. T., S. Vink, R. Wollast and L. Chou. 1995. Comparitive geochemistry of marine saline lakes. In Lerman, A., D. M. Imboden and J. R. Gat (eds). Physics and Chemistry of Lakes. Springer-Verlag, Berlin.

Marker, M. E. 1981. Karst in the Bredasdorp area: a preliminary analysis. *SA Geographer* 9:25-29.

Mason, B. and C.B. Moore. 1982. Principles of Geochemistry (4th edition). John Wiley and Sons, New York.

McBride, M.B. 1994. Environmental Chemistry of Soils. Oxford University Press, New York.

McQuaid. 1996. Primary productivity of De Hoop Vlei, South Africa. Unpublished Research Report, University of Cape Town.

Meybeck, M. 1995. Global distribution of lakes. In Lerman, A., D. M. Imboden and J. R. Gat (eds). Physics and Chemistry of Lakes. Springer-Verlag, Berlin.

Muller, G. and Gastner, M. 1971. The Karbonat-Bombe, a simple device for the determination of the carbonate content in sediments, soils and other minerals. *N. Jb. Mineral* 10:466-469.

Noble, R. G. and J. Hemens. 1978. Inland Water Ecosystems of South Africa - a Review of Research Needs. South African Narional Scientific Programmes Report No 34. CSIR.

Non-Affiliated Soil Analysis Work Committee. 1990. Handbook of Standard Soil Testing Methods for Advisory Purposes. Soil Science Society of South Africa, Pretoria.

Nordstrom, D.K. and J.L. Munoz. 1994. Geochemical Thermodynamics (2nd edition). Blackwell Scientific, Cambridge.

Olsen, S.R. and L.E. Sommers. 1982. Phosphorus In Page, A.L. (ed) Methods of Soil Analysis, Part II, chemical and microbiological properties (2nd edition). Soil Science Society of America, Madison.

PD Toens and Associates. 1994a. De Hoop Nature Reserve: groundwater management and monitoring progress report no. 1. A geohydrological investigation of the De Hoop Nature Reserve.

PD Toens and Associates. 1994b. Report on the evaluation of the historical chemical data of the De Hoop Vlei water at the gauging station.

PD Toens and Associates. 1996. De Hoop Nature Reserve: groundwater management and monitoring progress report no. 6 for the period February 1996 to September 1996.

Rawlins, B.G., J.P. Reader, B.Smith and N. Breward. 1997. Modelling and mapping the concentration and mobility of potentially toxic elements in Welsh streamwaters using national hydrochemical survey data. Proceedings of the Society for Environmental Geochemistry and Health 15th European conference on Mining and the Environment. Dublin.

Renaut, R.W. 1990. Recent carbonate sedimentation and brine evolution in the saline lake basins of the Cariboo Plateau, British Columbia, Canada. *Hydrobiologia* 197:67-81.

Reuter, J.E., C.L. Rhodes, M.E. Lebo, M. Kotzman and C.R. Goldman. 1993. The importance of nitrogen in Pyramid Lake (Nevada, USA), a saline desert lake. *Hydrobiologia* 267:179-189.

Reznikov, S.A. and D.S. Turovskii. 1983. New data on the mineralogical composition and distribution of carbonates in bottom sediments of Lake Sevan. *Chemical Abstracts* 102:11958.

Rivadeneyra, M.A., R. Delgado, G. Delgado, A. Del Moral, M.R. Ferrer and A. Ramos-Cormenzana. 1994. Precipitation of carbonates by *Bacillus* sp. isolated from saline soils. *Geomicrobiology Journal* 11:175-184.

Rosen, M.R., J.V. Turner, L. Coshell and V. Gailitis. 1995. The effect of water temperature, stratification , and biological activity on the stable isotopic composition and timing of carbonate precipitation in a hypersaline lake. *Geochimica et Cosmochimica Acta* 59:979-990.

Scott, A. 1995. De Hoop Nature Reserve: Jewel of the Western Cape. Informational Booklet. Cape Nature Conservation, Cape Town.

Scott, H. A. and K. C. D. Hamman. 1988. Recent fish records from De Hoop Vlei, a southern Cape coastal lake. *Bontebok* 6:30-33.

Seaman, M. T., P. J. Ashton and W. D. Williams. 1991. Inland salt waters of southern Africa. *Hydrobiologia* 210:75-91.

Shaw, P.A. and D.S.G. Thomas. 1989. Playas, pans and salt lakes. In Thomas, D.S.G. (ed). Arid Zone Geomorphology. Belhaven Press, London.

Smith, C.L. and J.I. Drever. 1976. Controls on the chemistry of springs at Teels Marsh, Mineral County, Nevada. *Geochimica et Cosmochimica Acta* 40:1081-1093.

Snoeyink, V.L. and D. Jenkins. 1980. Water Chemistry. John Wiley & Sons, New York.

Soil Classification Working Group. 1991. Soil Classification: a taxonomic system for South Africa. Memoirs on the Agricultural Natural Resources of South Africa No. 15. Department of Agricultural Development, Pretoria.

Standard Methods. 1985. Standard Methods for the Examination of Water and Wastewater (16th edition). American Public Health Association, Washington DC.

Truswell, J.F. 1977. The Geological Evolution of South Africa. Purnell, Johannesburg.

van der Spuy, D. and J.P. Willis. 1991. The occurrence of aragonite in carbonate lenses in coals from the Witbank area. *South African Journal of Geology* 94:178-180.

van Vliet, H.R.P., P.L. Kempster, D.P. Sartory, F.A. Gerber and I.J. Schoonraad. 1988. Analytical methods manual. Hydrological Research Institute Report No. TR136. South African Department of Water Affairs, Pretoria.

Velbel, M.A., D.T. Long and J.L. Gooding. 1991. Terrestrial weathering of Antarctic stone meteorites: formation of Mg-carbonates on ordinary chondrites. *Geochimica et Cosmochimica Acta* 55:67-76.

Vieillard, P. and Y. Tardy. 1984. Thermochemical properties of phosphates. In Nriagu, J.D. and P.B. Moore (eds). Phosphate minerals. Springer-Verlag, Berlin.

Walkley, A. 1935. An examination of methods for determining organic carbon and nitrogen in soils. Journal of Agricultural Science 25:598-609.

Warren, J.K. 1990. Sedimentology and mineralogy of dolomitic Coorong lakes, *South Australia. Journal of Sedimentary Petrology* 60:843-858.

Wehmiller, J. 1972. Strontium: element and geochemistry. In Fairbridge, R.W. (ed) The Encyclopedia of Geochemistry and Environmental Sciences. Van Nostrand Reinhold Company, New York.

Wetzel, R. G. 1983. Limnology, 2nd edition. Saunders College Publishing, Orlando.

Whittig, L.D. and W.R. Allardice. 1986. X-ray diffraction techniques. In Klute, A. Methods of Soil Analysis, Part I, physical and mineralogical methods (2nd edition). Soil Science Society of America, Madison.

Williams, W. D. 1993. Conservation of salt lakes. *Hydrobiologia* 267:291-306.

Williams, W. D. 1996. What future for saline lakes. *Environment* 38:12-20.

Willis, J.P. 1995. Instrumental parameters and data quality for routine major and trace element determinations by WDXRFS. Information circular No. 14. Department of Geological Sciences, University of Cape Town.

Zheng, M., J. Tang, J. Liu and F. Zhang. 1993. Chinese saline lakes. *Hydrobiologia* 267:23-36.

Zheng, X. and S. Yang 1983. Components of the saline lake water in Tibet. *Chemical Abstracts* 101:11869.

Appendix 1 Analytical appraisal

A1.1 Precision

To test the precision of analyses the following procedures were followed. Certain water samples were collected and analyzed in duplicate. During analytical runs certain samples were analyzed in duplicate or triplicate. Relative standard deviations were calculated for the results of these repetition analyses. These relative standard deviations are presented in Table A1.1. The results of RSD calculations indicate acceptable levels of precision for the purposes of this study.

Table A1.1 Relative standard deviations (RSD) calculated for repeated analyses. The range of RSD values calculated for each method of analysis are shown. The first column are RSD values calculated for analyses of duplicate samples. The second column are those calculated for repeat analyses of the same sample.

Analysis	RSD (%)	
	Duplicate samples	Repetitions
EC	0.0 - 1.3	0.0 - 0.7
pH	0.0 - 0.5	0.0 - 0.7
Alkalinity	0.1 - 1.1	0.1 - 2.1
P	0.4 - 9.2	0.3 - 5.5
F	0.0 - 1.3	
HPIC analyses		
Ca		5.6
Mg		7.2
Na		3.5
K		3.3
Cl	0.9 - 3.3	1.8
SO_4	0.8 - 2.0	9.5
ICP analyses		
Ca	0.2 - 2.2	
Mg	0.2 - 5.4	
Na	0.6 - 1.8	
K	0.8 - 5.9	
Si	0.3 - 10.3	2.1 - 16.2
Organic C		0.4 - 8.2
Carbonate		0.2 - 2.8

1.2 Accuracy

The cation-anion charge balance is an excellent test of the quality of major ion data for aqueous solutions since all aqueous systems must be electrically neutral (Drever, 1988). A charge balance was calculated on all water samples using the equation

$$\text{Charge balance} = [\,(\Sigma\text{cations} - \Sigma\text{anions})/(\Sigma\text{cations} + \Sigma\text{anions})\,] \times 100$$

The results of these calculations are presented in Table A1.2. All charge balances are within 10 percent, indicating an acceptable level of accuracy for the major ion data.

Table A1.2

Sample	Charge balance
M3	3.5
M5	-0.2
M5-2	6.1
M6	0.7
D3-2	4.5
D4-2	5.0
H1	1.0
H1-2	8.0
H4	6.6
T1	-1.4
T2	-3.5
T3	0.0
W7-2	8.5
W3-2	9.9
W2-2	7.1
P1	0.8
P2	0.6
P4	0.8
S4-2	8.1
S1	-1.5
S1-2	9.1
S2	5.3
S3	0.3
DF	0.3
IM3-100	4.6
IM5-150	7.7
IT2-210	9.1

During EC, pH, P, F and carbonate determinations, standards were analyzed. The results of these analyses indicated acceptable levels of accuracy for these analytical methods. The accuracy of XRF data was checked by summation of all major oxides, CO_2, organic matter and H_2O and comparison of the sum to 100%. The XRF analyses used in the results of the study were those which showed errors of less than 7 percent, when checked in this way. Information about the precision, accuracy and instrumental set-up for XRF analyses are given in Willis (1995).

DWAF water quality data for De Hoop Vlei monitoring station

Date	Main Reading (m)		EC (mS/m)	TDS	pH	Na	Mg	Ca	F	Cl	N (NO3 + NO2)	SO4	P	CaCO3 alkalinity	Si	K	N (NH4)
650730	4.801	0	1200		7.6	2185	255	110	0.6	3830	0.00	360		305			
650730	4.801	0	1222		7.3	2300	255	100	0.6	3980	0.00	384		310			
651217	4.45	0	2222		8.0	4940	485	140	1.3	8555	0.68	624		600			
651217	4.45	0	1333		7.7	2650	304	40	0.9	4370	0.00	384		350			
651218	4.45	0	1333		7.5	2480	316	60	0.8	4370	0.00	336		300			
670503	0.235	0	689		7.6	1309	169	70	0.5	2311	9.71	240		135			
690113	3.908	0	1667		8.9	2869	463	160		5680	0.00	96		283			
690113	3.841	0	1667		9.2	3151	292	120		5502	0.00	96		244			
690127	3.816	0	1500		9.3	2760	340	120		5290	0.00	0		233			
690127	3.816	0	1500		9.0	2830	370	140		5250	0.00	290		290			
690210	3.621	0	1556		8.6	3036	357	104		5502	0.00	288		290			
690210	3.621	0	1556		8.7	3013	363	92		5502	0.00	240		274			
690602	3.347	0	1725		8.8	3270	370	150		6400	0.00	280		265			
690602	3.347	0	2014		8.9	3370	400	100		6450	0.00	280		187			
690616	3.344	0	2000		9.0	3651	340	240		6820	0.00	96		263			
690616	3.344	0	2000		8.9	3600	420	200		6820	2.03	96		315			
690703	3.35	0	1556		8.5	3606	380	120		5960	0.00	480		285			
690703	3.35	0	1611		8.7	3828	390	120		6820	0.00	576		253			
690807	3.301	0	1556		8.8	3529	370	120		6180	0.00	480		270			
690807	3.301	0	1556		8.8	3080	207	60		5860	1.36	760		272			
710906	3.627	0	556		8.1	1066	122	132	0.0	1845		314		227			
710906	3.627	0	789		7.9	1457	178	227	0.0	2614	11.97	521		196			
710906	3.627	0	939		8.0	1803	214	273	0.0	3148	9.71	670		265			
770201	3.25	0	909	5494	7.1	1607	198	148	1.0	2725	1.46	597	0.16	151	1.42	27	0.05
770207	3.2	0	918	5573	7.2	1655	204	127	1.0	2776	0.05	602	0.04	151	0.81	24	0.06
770214	3.17	0	917	5522	7.2	1607	204	129	1.0	2765	0.03	602	0.03	155	0.61	23	0.05
770221	3.18	0	767	4638	7.2	1311	173	112	0.8	2280	1.07	493	0.14	194	5.28	27	0.05
770228	3.11	0	928	5374	7.9	1590	172	170	1.1	2685	0.70	620	0.09	85	0.11	30	0.00
770307	3.08	0	931	5480	8.1	1612	203	139	1.2	2734	0.59	622	0.09	113	0.07	28	0.01
770314	3.01	0	937	5575	8.0	1631	206	138	1.3	2775	0.19	638	0.06	131	0.04	25	0.05
770322	2.98	0	955	5550	7.3	1642	206	138	1.3	2744	0.27	640	0.07	124	0.06	26	0.15
770328	2.95	0	718	5750	8.8	1688	196	128	1.0	2887	0.07	698	0.06	98	0.07	32	0.18
770404	2.93	0	762	5657	7.0	1660	198	127	1.0	2849	1.17	690	0.17	80	0.12	29	0.05
770412	2.93	0	344	2174	7.1	624	79	43	0.6	1020	1.78	257	0.28	101	0.05	19	0.03
770418	2.94	0	960	5611	8.8	1679	203	133	1.2	2764	0.08	664	0.13	114	0.11	27	0.10

Date	Main		EC	TDS	pH	Na	Mg	Ca	F	Cl	N	SO4	P	CaCO3	Si	K	N
770425	3.12	0	930	6561	7.1	1447	404	310	1.2	2790	1.88	1334	0.28	183	0.90	44	0.06
770502	3.18	0	946	6741	7.0	1492	401	329	1.3	2867	2.52	1348	0.36	200	1.40	48	0.14
770509	3.21	0	836	6128	7.3	1252	407	318	1.0	2438	3.92	1411	0.10	194	1.59	47	0.06
770516	3.36	0	964	6651	8.7	1599	387	248	1.2	3009	0.54	1143	0.10	176	0.26	47	0.07
770603	3.55	0	942	6000	7.4	1715	195	139	1.0	2815	0.00	855	0.02	211	0.63	24	0.27
770805	4.86	0	717	4476	7.7	1370	168	58	1.0	2201	0.37	349	0.05	254	0.34	17	0.04
770815	4.93	0	752	4571	7.9	1384	175	61	1.1	2268	0.09	360	0.03	250	0.17	18	0.04
770822	5.04	0	741	4499	7.7	1348	173	57	1.1	2230	0.16	357	0.05	259	0.54	17	0.06
770829	5.06	0	741	4447	8.0	1343	141	58	1.1	2221	0.12	353	0.05	258	0.12	17	0.06
770906	5.05	0	761	4643	7.5	1382	161	76	0.9	2323	0.00	351	0.01	272	0.25	17	0.02
770912	5.06	0	745	4483	7.5	1363	162	77	0.9	2334	0.00	195	0.00	273	0.00	18	0.01
770919	5	0	769	4678	7.3	1384	162	77	0.9	2350	0.10	351	0.01	275	1.98	18	0.09
771005	4.91	0	779	4995	8.3	1447	169	128	1.0	2569	0.01	371	0.01	242	0.06	15	0.05
771017	4.88	0	788	4966	8.2	1460	172	109	1.0	2571	0.01	366	0.02	224	0.49	15	0.05
771026	4.78	0	810	5158	9.1	1534	177	106	1.0	2718	0.01	394	0.01	174	0.11	15	0.05
771106	4.67	0	798	5185	9.1	1525	176	111	1.1	2723	0.01	387	0.01	204	0.46	14	0.04
780124	4.128	0	953	5691	8.2	1764	201	61	1.1	3079	0.01	336	0.01	188	0.08	19	0.12
831116	2.28	0	1310	9040	8.6	2700	316	144	0.9	4755	0.01	934	0.02	136	0.82	25	0.12
831124	2.23	0	1337	9202	8.6	2865	321	155	0.9	4755	0.02	922	0.02	131	0.41	25	0.11
831215	2.2	0	1404	9542	10.0	3038	342	127	0.9	5019	0.00	881	0.01	83	0.62	33	0.06
840115	0	0	1602	10671	9.0	3168	327	134	1.2	5921	0.03	787	0.02	44	1.51	278	0.15
840215	1.63	0	2196	13868	8.5	4362	437	242	1.5	7606	0.03	1144	0.03	29	0.93	40	0.20
840918	1.15	0	985	6209	8.2	1667	222	238	0.4	3103	0.07	690	0.12	215	3.48	18	6.38
841016	1.12	1	1808	12159	7.8	3427	469	201	0.8	6124	0.25	1602	0.71	209	1.29	72	4.23
841113	1.01	1	942	5834	8.0	1624	184	227	0.5	2893	0.20	686	0.04	154	4.70	31	1.38
850730	2.08	1	518	3009	8.2	897	109	73	0.4	1483	2.47	243	0.08	145	5.64	15	0.17
850827	3.19	1	740	4011	8.8	1178	142	102	0.6	2005	0.35	321	0.22	192	1.85	24	1.10
850924	3.09	1	845	4428	8.6	1290	153	112	0.9	2207	0.50	363	0.12	225	1.08	25	0.14
851022	2.92	1	800	4929	7.9	1377	174	145	0.8	2388	0.24	518	0.07	238	2.12	35	0.02
851119	2.76	1	860	5121	7.9	1445	185	134	0.9	2572	0.02	468	0.02	239	1.57	25	0.03
851217	2.6	1	980	5540	8.3	1585	197	146	1.0	2788	0.02	530	0.04	224	0.92	21	0.08
860114	2.35	1	1036	5961	7.7	1750	209	111	0.8	3162	0.00	583	0.01	98	1.75	27	0.19
860211	2.1	1	1060	7146	8.0	2159	245	136	0.9	3489	0.01	911	0.07	102	1.04	81	0.22
860311	1.96	1	1200	7541	8.8	2269	253	140	0.7	3824	0.01	824	0.09	143	1.24	55	0.98
860408	1.81	1	1200	7304	8.8	2121	245	154	0.8	3810	0.03	686	0.08	197	2.67	47	0.70
860506	1.71	1	1390	8731	8.2	2585	293	196	0.6	4446	0.01	1014	0.04	111	0.39	60	0.21
860603	1.6	1	1090	7220	7.7	1995	235	210	0.7	3574	0.02	739	0.10	341	9.87	49	0.37
860701	1.54	1	1160	7308	8.9	2292	242	170	0.7	3744	0.04	704	0.04	105	0.61	26	0.14
860729	1.51	1	900	5578	9.0	1565	197	135	0.7	2887	0.00	637	0.02	98	0.26	35	0.11
860826	1.5	1	710	4292	8.7	1253	147	116	0.6	2149	0.03	485	0.02	100	0.86	21	0.08

Date	Main		EC	TDS	pH	Na	Mg	Ca	F	Cl	N	SO4	P	CaCO3	Si	K	N
860923	4.71	1	358	2065	6.8	613	65	45	0.6	1024	0.26	140	0.20	131	4.99	15	0.37
861021	4.615	1	506	2819	7.8	854	98	65	0.6	1396	0.10	186	0.11	164	3.24	20	0.07
861118	4.42	1	602	3209	8.0	930	111	71	0.7	1615	0.25	205	0.17	209	3.99	22	0.16
870113	3.89	1	666	3953	8.2	1121	137	89	0.8	1998	0.00	261	0.07	261	3.63	27	0.17
870210	3.63	1	720	4220	8.9	1263	140	79	0.8	2143	0.03	277	0.09	239	1.27	26	0.14
870310	3.46	1	761	4465	8.5	1299	157	71	0.8	2301	0.03	319	0.06	240	1.35	24	0.12
870407	3.3	1	820	4558	8.6	1356	159	70	0.8	2361	0.04	276	0.06	254	0.75	24	0.10
870505	3.3	1	760	4535	8.7	1381	158	67	0.8	2340	0.04	247	0.08	254	1.06	31	0.13
870602	3.2	1	750	7021	8.2	1398	163	774	0.8	2308	0.40	2050	0.07	244	2.14	28	0.24
870630	3.18	1	760	4649	7.9	1381	164	75	0.9	2412	0.03	284	0.06	251	0.73	27	0.15
870728	3.1	1	800	4613	8.1	1403	160	73	0.8	2439	0.03	198	0.02	257	0.34	26	0.10
870825	3.07	1	770	4603	8.0	1383	166	79	0.9	2385	0.10	243	0.05	265	0.97	22	0.49
870929	2.985	1	750	4587	8.5	1397	163	67	0.7	2424	0.04	240	0.03	225	0.34	21	0.18
871027	2.84	1	776	4744	9.4	1502	162	47	0.7	2521	0.02	281	0.04	169	0.54	24	0.09
871124	2.65	1	881	5028	9.5	1579	162	64	0.6	2728	0.03	312	0.02	132	0.58	23	0.03
871222	2.46	1	967	5359	9.1	1698	162	65	0.7	2913	0.01	344	0.03	120	0.59	30	0.07
880119	2.25	1	1082	5958	8.4	1931	184	89	0.6	3287	0.02	283	0.00	127	0.55	30	0.06
880216	2.07	1	1168	6801	8.9	2140	208	103	0.6	3764	0.02	387	0.00	141	1.18	27	0.08
880311	1.965	1	1140	6637	9.0	2072	200	99	0.7	3712	0.05	324	0.06	167	3.67	26	0.14
880412	0.885	1	1210	6921	9.2	2155	212	82	0.7	3794	0.04	375	0.05	218	1.33	36	0.12
880510	1.805	1	1240	7426	9.4	2328	235	105	0.8	4114	0.06	325	0.04	231	0.69	38	0.12
880607	1.77	1	1080	6240	9.1	1959	208	74	0.8	3366	0.01	286	0.07	261	1.24	28	0.12
880705	1.745	1	950	5860	8.8	1818	207	84	0.7	3227	0.04	118	0.13	306	0.85	32	0.35
880802	1.7	1	992	6183	8.9	1867	215	96	1.0	3168	0.07	410	0.15	324	1.17	30	0.46
880830	1.68	1	905	5320	9.1	1609	211	78	1.0	2802	0.05	236	0.09	294	1.02	25	0.14
880927	1.603	1	872	5022	8.9	1490	177	82	0.8	2624	0.09	335	0.03	238	0.94	23	0.12
881025	1.48	1	960	5780	8.7	1755	193	125	0.8	3101	0.05	303	0.07	229	1.03	23	0.23
881129	1.27	1	1620	9779	8.5	3100	326	114	0.0	5240	0.02	616	0.05	285	1.37	35	0.33
881220	1.13	1	1632	10564	7.5	3324	369	152	0.5	5632	0.03	634	0.48	310	1.47	71	1.75
890509	1.305	1	632	4068	8.0	1044	136	186	0.6	1799	0.04	627	0.03	204	0.76	27	0.23
890606	1.343	1	764	5181	8.4	1275	188	269	0.7	2269	0.06	842	0.02	254	0.88	27	0.35
890704	2.7	1	647	4024	8.6	1164	146	109	0.6	1934	0.33	401	0.05	200	2.36	22	0.57
890801	2.885	1	590	4054	8.4	1127	138	112	0.6	1975	0.28	397	0.04	232	1.76	20	0.57
890829	3.26	1	762	4738	8.2	1387	172	130	0.7	2296	0.25	379	0.07	287	1.62	23	0.01
890926	3.51	1	736	4998	7.2	1435	176	114	0.8	2370	0.13	504	0.04	310	0.81	20	0.16
891024	3.45	1	746	5054	8.7	1456	177	113	0.7	2500	0.02	435	0.04	288	0.33	21	0.06
891121	3.29	1	683	5014	9.4	1491	178	86	0.7	2610	0.00	373	0.02	211	1.07	18	0.07
891219	3.04	1	910	5452	9.7	1690	204	73	0.8	2833	0.05	410	0.04	179	0.69	23	0.10
900116	2.79	1	875	5904	9.8	1803	202	90	0.8	3146	0.00	442	0.02	165	0.59	21	0.09
900410	2.265	1	1021	7312	9.7	2296	246	117	0.6	3942	0.04	419	0.01	215	1.00	29	0.03

Date	Main		EC	TDS	pH	Na	Mg	Ca	F	Cl	N	SO4	P	CaCO3	Si	K	N
900508	2.305	1	977	6570	8.3	2106	226	104	0.6	3555	0.03	301	0.10	208	1.29	25	0.14
900605	2.265	1	875	6618	9.4	2008	220	91	0.7	3628	0.03	351	0.16	241	1.20	25	0.12
900703	2.6	1	981	6463	9.4	1869	290	126	0.7	3247	0.02	531	0.11	307	0.73	25	0.11
900731	3.285	1	737	5025	8.9	1508	177	73	0.7	2545	0.01	334	0.02	304	0.49	17	0.19
900828	3.29	1	760	5582	9.7	1695	200	90	0.8	2798	0.07	380	0.15	325	0.49	20	0.28
900925	3.22	1	845	5374	10.0	1653	190	69	0.7	2787	0.04	317	0.07	281	0.52	15	0.12
901023	3.045	1	858	5771	10.1	1776	211	67	0.7	3014	0.02	359	0.04	270	0.83	15	0.09
901120	2.855	1	1016	6270	10.0	1952	207	58	0.7	3315	0.02	405	0.06	253	1.19	24	0.07
901218	2.64	1	1078	6707	9.9	2149	239	66	0.6	3588	0.01	352	0.04	243	1.00	18	0.11
910115	2.24	1	1173	7100	10.2	2266	213	54	0.7	3920	0.05	333	0.03	242	0.91	18	0.12
910212	2.255	1	1300	7778	9.5	2479	247	89	0.6	4317	0.03	262	0.04	295	1.33	23	0.54
910312	2.12	1	1370	8977	9.6	2843	297	83	0.7	4947	0.02	396	0.03	312	1.10	30	0.12
910409	1.95	1	1470	9731	9.5	3058	331	95	0.8	5426	0.02	380	0.06	339	0.86	27	0.22
910507	1.85	1	1480	9452	9.4	2973	321	83	0.8	5232	0.02	344	0.10	385	0.85	29	0.18
910604	1.785	1	1340	9543	9.1	2912	348	79	0.9	5191	0.06	430	0.20	457	1.10	24	0.45
910702	1.76	1	1287	8127	9.2	2590	300	75	1.1	4282	0.02	264	0.24	482	0.97	26	0.18
910730	1.73	1	1086	7350	9.0	2216	264	93	1.1	3606	0.09	242	0.28	741	2.54	23	0.40
910827	1.665	1	1170	7385	8.8	2215	275	84	1.1	3901	0.03	246	0.19	523	2.40	23	0.68
911021	1.5	1	1141	7801	9.1	2401	265	72	1.1	4082	0.03	149	0.40	655	4.70	30	0.36
911118	1.41	1	1192	7497	9.7	2363	268	31	1.0	4008	0.00	221	0.21	473	3.91	29	0.19
930917	1.6	1	677	4624	8.3	1321	173	96	0.8	2256	0.08	310	0.11	366	2.14	18	0.85
931015	1.488	1	802	5054	8.3	1457	190	128	1.0	2422	0.48	344	0.16	400	2.13	21	0.67
931115	1.24	1	861	5821	8.5	1627	226	173	0.9	2754	0.16	443	0.12	467	1.38	25	0.32
940112	0	1	1041	5721	7.8	1724	203	104	0.8	2702	0.11	743	0.23	174	1.90	33	0.26
940214	0.607	1	1203	7157	10.0	2190	224	94	0.9	3846	0.07	608	0.16	134	0.66	31	0.26
940315	0.44	1	1310	8083	8.7	2516	267	158	1.0	4212	0.04	563	0.19	247	1.85	62	1.87
940415	0.265	1	1270	8387	8.9	2548	286	158	0.9	4328	0.04	654	0.13	290	0.78	57	0.61
940516	0.19	1	991	6514	8.8	1892	260	137	1.0	3137	0.12	684	0.16	313	3.75	20	0.54
940612	0.164	1	829	5403	9.2	1516	195	144	0.8	2595	0.07	588	0.11	290	3.12	8	0.66
940713	1.24	1	448	2777	8.5	788	90	62	0.9	1338	5.83	213	0.08	198	4.52	17	0.11
940816	1.81	1	721	4234	8.4	1232	178	80	0.7	2085	0.02	271	0.06	293	0.65	29	0.22
941006	1.99	1	829	5143	8.3	1533	189	95	1.0	2550	0.45	275	0.14	385	2.15	28	0.25
941105	1.76	1	946	5685	9.0	1651	195	162	0.8	2819	0.02	303	0.10	448	1.53	8	0.05
950104	1.498	1	835	5444	9.9	1736	169	38	0.4	2940	0.07	313	0.07	178	0.65	30	0.14
950208	1.215	1	1022	6268	9.9	1982	174	62	0.4	3409	0.03	377	0.07	184	0.51	39	0.10
950306	1.03	1	1107	6690	9.6	2132	188	72	0.5	3681	0.03	288	0.03	220	0.19	60	0.08
950406	1	1	946	5476	10.3	1785	166	52	0.4	3173	0.03	16	0.10	196	0.28	44	0.38
950505	0.943	1	918	5499	9.7	1760	168	75	0.5	2844	0.01	272	0.19	267	0.33	53	0.78
950607	0.72	1	796	4829	9.8	1525	165	50	0.6	2464	0.02	190	0.21	332	0.49	29	0.35
950704	0.91	1	730	4866	9.9	1409	169	63	0.7	2393	0.02	219	0.27	477	0.49	29	0.42

Date	Main		EC	TDS	pH	Na	Mg	Ca	F	Cl	N	SO4	P	CaCO3	Si	K	N
950807	1	1	1117	6653	9.3	2031	258	81	0.7	3345	0.01	313	0.24	470	0.35	50	0.53
950907	1.18	1	1114	7124	9.4	2160	250	76	0.8	3703	0.04	424	0.10	378	0.44	49	0.34
951011	1.17	1	1227	7680	9.9	2375	243	83	0.8	3970	0.03	432	0.11	399	0.54	89	0.09
951110	2.487	1	1370	7837	10.0	2567	242	54	0.7	4190	0.06	371	0.08	288	0.26	60	0.08

TABLE 11: DE HOOP VLEI INFORMATION

TOENS & PARTNERS cc
GEOLOGICAL , HYDROGEOLOGICAL & ENGINEERING CONSULTANTS

				VLEI 1 (De Hoop Camp)				VLEI 2 (Aasvoëlkrans)				VLEI 3 (De Mond)			
MONTH	SAMPLING DATE	RAIN-FALL (mm)	WATER DEPTH (m)	E.C. (mS/m)	Ca (mg/l)	Mg (mg/l)	HARDNESS (CaCO3) (mg/l)	E.C. (mS/m)	Ca (mg/l)	Mg (mg/l)	HARDNESS (CaCO3) (mg/l)	E.C. (mS/m)	Ca (mg/l)	Mg (mg/l)	HARDNESS (CaCO3) (mg/l)
Feb		41.0	0.60	1110	102	226	1187	2250				1109			
Mar		20.5	0.44												
Apr		40.1	0.26												
May	06/06/1994	0.0	0.23	760	128	21	406	2600	57.0	18	215	1160	69.4	30	298
Jun	04/07/1994	73.4	0.48	1040	148	241	1362	385	41.0	79	429	1180	74.2	263	1268
Jul	01/08/1994	33.7	1.68	650	83	136	318	790	76.0	170	889	810	76.0	169	885
Aug	05/09/1994	45.4	2.14	800	90	178	957	940	80.0	211	1069	800	74.0	174	902
Sep	04/10/1994	12.8	1.80	880	101	197	1062	1100	92.0	248	1250	920	80.0	183	953
Oct	07/11/1994	29.3	1.65	960	109	208	1130	1240	77.0	243	1192	880	79.0	190	979
Nov	05/12/1994	1.0		1030	60	224	1074	1330	80.0	268	1302	960	60.0	202	980
Dec	09/01/1994	153.5	1.48	980	52	194	927	1290	83.0	248	1228	1000	58.0	201	971
Jan	07/02/1995	10.2													
Feb	13/03/1995	16.7	1.10	1130	65	195	964	1250	74.0	227	1120	1180	61.0	208	1007
Mar	10/04/1995	82.1	1.00	1000	54	183	891	1200	50.0	222	1039	1140	53.0	200	956
Apr	08/05/1995	60.4		860	58	164	820	1050	41.0	230	1050	1100	49.0	220	1029
May	19/06/1995	49.0	1.00	820	59	181	891	1280	104.0	322	1584	1120	53.0	226	1064
Jun	03/07/1995	43.0	1.00	765	62	186	920	1600	111.0	399	1921	1100	53.0	233	1091
Jul	06/08/1995	33.3	1.20	1120	95	284	1404	1210	102.0	297	1476	1110	62.0	228	1092
Aug		43.2													
Sep		26.6													
Oct	26/10/1995	13.5		1290	61	308	1421	1340	92.0	323	1559	1210	60.0	265	1242
Nov		4.2													
Dec		103.8													
Jan	16/01/1996	18	0.70	1650	73	314	1477	1850	63.0	424	1903	1500	59.0	294	1356
Feb		19	0.50												
Mar		12	0.20												
Apr		9	0.00												
May	24/05/1996	11	0.00	1200	124	346	1733	3650	58.0	1034	4404	1950	62.0	444	1984
Jun		22	0.00												
Jul	11/07/1996	70	0.00	640	175	140	1015	1950	53.0	441	1948	2150	56.0	504	2216
Aug	09/09/1996	16	0.00												
Sep		28	0.00												
Oct	31/10/1996	98	0.00					2950	48.9	792	3384	2250	48.3	506	2203
Nov		60													
Dec	17/12/1996	25	0.00												
Jan	22/01/1997	2	0.00									2650	55.0	638	2764
Feb	24/02/1997	22	0.00					2850	45.0	760	3239	4050	68.0	1075	4593
Mar	25/03/1997	34						3300	58.6	863	3697	5300	52.3	1467	6166
Apr		36													

Water depth measured at gauging station, De Hoop Camp.

TABLE 12: DE HOOP VLEI INFORMATION

TOENS & PARTNERS cc
GEOLOGICAL , HYDROGEOLOGICAL & ENGINEERING CONSULTANTS

				VLEI 1 (De Hoop Camp)			VLEI 2 (Aasvoelkrans)			VLEI 3 (De Mond)		
MONTH	SAMPLING DATE	RAIN-FALL (mm)	WATER DEPTH (m)	AMMONIA N (mg/l)	NITRATE N (mg/l)	PHOSPHATE P (mg/l)	AMMONIA N (mg/l)	NITRATE N (mg/l)	PHOSPHATE P (mg/l)	AMMONIA N (mg/l)	NITRATE N (mg/l)	PHOSPHATE P (mg/l)
Feb		41.0	0.60									
Mar		20.5	0.44									
Apr		40.1	0.26									
May	06/06/1994	0.0	0.23		0.73	0.10		4.36	0.59		0.19	0.10
Jun	04/07/1994	73.4	0.48		2.26	0.17		9.88	0.10		0.15	0.10
Jul	01/08/1994	33.7	1.68		1.00	0.10		2.26	0.10		2.79	0.10
Aug	05/09/1994	45.4	2.14	0.44	0.10	0.05	0.05	0.10	0.05	0.46	0.57	0.05
Sep	04/10/1994	12.8	1.80	0.57	0.36	0.17	0.10	0.10	0.10	0.63	0.25	0.10
Oct	07/11/1994	29.3	1.65	0.10	0.10	0.10	0.29	0.10	0.10	0.10	0.10	0.10
Nov	05/12/1994	1.0		0.10	0.10	0.10	0.55	0.10	0.10	0.10	0.10	0.10
Dec	09/01/1994	153.5	1.48	0.10	0.10	0.10	0.29	0.10	0.10	0.10	0.10	0.10
Jan	07/02/1995	10.2										
Feb	13/03/1995	16.7	1.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Mar	10/04/1995	82.1	1.00	0.09	0.10	0.10	0.12	0.10	0.10	0.29	0.10	0.10
Apr	08/05/1995	60.4		0.11	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
May	19/06/1995	49.0	1.00	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Jun	03/07/1995	43.0	1.00	0.10	0.10	0.20	0.10	0.10	0.10	0.10	0.10	0.10
Jul	06/08/1995	33.3	1.20	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Aug		43.2										
Sep		26.6										
Oct	26/10/1995	13.5		0.37	0.10	0.10	0.45	0.10	0.21	0.30	0.10	0.10
Nov		4.2										
Dec		103.8										
Jan	16/01/1996	18	0.70	5.80	0.10	1.07	0.66	0.10	0.10	0.37	0.10	0.10
Feb		19	0.50									
Mar		12	0.20									
Apr		9	0.00									
May	24/05/1996	11	0.00		1.52	0.16		2.64	0.84		0.10	0.10
Jun		22	0.00									
Jul	11/07/1996	70	0.00		2.58	0.59		0.94	0.15		0.10	0.10
Aug	09/09/1996	16	0.00									
Sep		28	0.00									
Oct	31/10/1996	98	0.00					1.00	0.05		0.40	0.05
Nov		60	0.00									
Dec	17/12/1996		0.00									
Jan	22/01/1997		0.00								1.50	0.05
Feb	24/02/1997	22	0.00					0.10	0.30		0.10	0.20
Mar	25/03/1997	34	0.00					0.10	0.70		0.10	0.20
Apr		36										

Water depth measured at water depth station at De Hoop Camp.

Appendix 4 Major ion speciation of water samples

Table A4.1 Speciation of the major ions calculated using MINTEQA2. Values are given as percentage of the total ion concentration used as input to the speciation programme.

Ion	Species	M5-2	M6	H1-2	T1	W3-2	IM3	IT2
Na^+	Na^+	98.7	98.4	98.5	99.8	99.0	98.7	98.1
	$NaSO_4^-$			1.3				1.7
Mg^{2+}	Mg^{2+}	87.4	84.1	88.6	95.9	91.5	88.0	77.1
	$MgCO_3^0$	6.8	10.0				2.6	
	$MgHCO_3^+$			1.4	2.2	2.2	6.3	2.3
	$MgSO_4^0$	4.9	4.9	9.4	1.2	5.4	3.1	20.5
Ca^{2+}	Ca^{2+}	84.3	79.9	87.3	95.6	90.6	87.1	75.0
	$CaCO_3^0$	9.7	14.2		1.1	1.3	3.8	
	$CaHCO_3^+$			1.2	1.9	2.0	5.6	2.0
	$CaSO_4^0$	5.4	5.4	10.6	1.4	6.1	3.5	22.8
K^+	K^+	99.1	99.1	98.1	99.9	99.0	99.4	97.7
	KSO_4^-			1.9		1.0		2.3
NH_4^+	NH_4^+						93.4	95.2
	NH_3^0						5.6	
	$NH_4SO_4^-$							4.1
SO_4^{2-}	SO_4^{2-}	57.1	66.5	47.6	83.9	50.7	57.6	69.4
	$MgSO_4^0$	18.5	14.2	27.5	2.5	25.4	22.8	11.5
	$CaSO_4^0$	5.2		5.7	12.5	6.3	3.2	16.5
	$NaSO_4^-$	19.0	18.5	18.8	1.0	17.2	15.3	1.8
CO_3^{2-}	CO_3^{2-}	15.3	21.8	1.7		1.6	1.6	
	HCO_3^-	25.2	26.5	69.6	95.1	72.9	78.6	85.1
	$MgCO_3^0$	26.6	24.9	5.2		4.2	3.4	
	$MgHCO_3^+$	2.3	1.4	11.8		10.4	8.3	2.1
	$CaCO_3^0$	9.6	1.4	1.4		1.4		
	$CaHCO_3^+$			1.9	1.1	2.0		2.3
	$NaCO_3^-$	18.8	22.4	2.4		1.9	1.6	
	$NaHCO_3^0$	1.7	1.5	5.5		5.0	4.3	
	$H_2CO_3^0$				2.0			9.8

Appendix 5 Results of PCA analyses

STAT. FACTOR ANALYSIS	Factor Loadings (Unrotated) (sedrsw2g.sta) Extraction: Principal components (Marked loadings are > .700000)				
Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
SIO2	.86577*	-.393618	.115890	-.228430	.035938
TIO2	.98662*	-.082418	.085518	-.060426	.028110
AL2O3	.97496*	.055315	.088280	-.144658	-.018623
FE2O3	.95061*	.042706	-.017227	.165511	-.121789
MGO	-.16462	.706146*	.427970	-.346277	-.299292
CAO	-.98847*	-.099850	.005831	-.007919	-.058860
NA2O	-.50551	.406417	.625538	-.139403	.357601
K2O	.98790*	.037843	.105169	-.064655	-.009992
P2O5	-.72470*	.226549	.092092	.259759	-.351480
CL	-.46343	.549146	.566643	.012636	.302869
S	.07003	.623557	-.531848	-.489795	.042834
H2O	.73293*	.162567	.300409	.475295	-.118343
CO2	-.98588*	-.002922	.035734	-.048444	-.078204
OM	.08032	.677254	-.596182	.113125	.315115
SR	-.98584*	-.054359	.094584	.003823	-.073400
BA	.98326*	.064509	.092278	-.077772	-.047718
MN	.67011	.369210	-.047599	-.089365	-.491868
ZR	-.52695	-.663038	.027000	-.123690	.023443
RB	.99382*	.027747	.076299	.003939	-.004194
V	.99124*	.018146	.075631	-.048598	-.010359
CR	.98907*	-.030608	.065129	-.079066	-.007956
ZN	.98299*	.074408	.000508	-.043067	.017038
CU	.62097	.425521	-.111977	.430349	.161924
NI	.99225*	.082271	.022586	-.032522	.016233
Y	.96857*	-.166746	.051617	-.065722	.104374
PB	.94045*	.103214	-.076671	.047858	.012032
CO	.96508*	.036961	.029020	.077050	-.054536
NB	.97546*	-.139924	.093672	-.051801	.044574
TH	.96463*	-.081267	.036074	.004197	.114862
U	-.22008	.875657*	-.052842	.052694	-.075442
Expl.Var	20.70803	3.679892	1.745309	1.040432	.886795
Prp.Totl	.69027	.122663	.058177	.034681	.029560

STAT. FACTOR ANALYSIS	Factor Scores (sedrsw2g.sta) Rotation: Varimax normalized Extraction: Principal components				
Case	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
M1-90	-1.20298	-.73689	.27645	-.89412	-.69534
M1-255	-.02669	-.71207	.22050	-.23654	-.77037
M1-290	-.77611	-1.05738	.89132	.00631	-.46137
M2-160	-1.14272	-1.27954	.32284	-1.24654	-1.32992
M3-100	-1.28251	-.88258	.48393	-.79092	-.10165
M4-135	-.99215	-.46855	-1.84963	.00090	-.46108
M5-150	-1.23004	2.36348	-1.53586	1.86166	-1.20342
M6-70	-1.70068	-.85136	.06366	.64696	.50935
M7-160	-.50684	.50133	-1.69785	-.29942	.41347
M8-160	-1.65391	-.90489	.79156	.21476	.13675
M9-120	-1.21886	.76428	-.10958	.60073	.57593
M9-240	-.18235	.14221	-.16778	-.28540	.81610
M10-120	-.90954	.11961	-.62646	-.30509	.81288
D2-120	.53684	.90292	-.59604	-2.01465	1.36608
D3-100	.54590	.97260	-.92696	-1.47130	1.81373
D3-290	1.16318	-.05063	-.77327	-1.43328	-.77411
D4-90	1.05801	.27767	.04581	-1.18014	.48568
H1-65	.67331	.02064	.22501	1.40745	.62679
H2-110	.77380	.05581	-.77229	.90950	-.32436
H2-310	1.16286	-.72874	-.42676	-.32687	-1.04072
H3-70	.47901	.83829	-.92791	1.07652	-.73168
H4-80	-.04693	.17077	1.11371	.59001	2.46927
T5-110	.28513	1.42670	1.93044	-1.03134	-.12075
T6-120	.18037	2.50909	1.57505	-.73307	-2.14841
T2-210	.40384	.37656	1.86246	.54628	.21955
T7-140	.41507	.42001	1.26471	1.92501	.26609
T7-300	1.07681	-1.11094	.91910	.82566	.58827
W2-170	1.60265	-1.14164	-.16297	.41565	-.64447
W2-250	1.60081	-1.08450	-.45607	.37434	-1.24265
S1-G	.91470	-.85223	-.95713	.84697	.95034